Organometallic compound as polymerization catalyst(Dissertation_全文)

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CITATION:

Inoue, Shohei. Organometallic compound as polymerization catalyst. 京都大学, 1962, 工学博士

ISSUE DATE:

1962-06-19

URL:

https://doi.org/10.14989/74989

ORGANOMETALLIC COMPOUND AS POLYMERIZATION CATALYST

1962

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O R G A N O M E T A L L I C C O M P O U N D

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S h o h e i I n o u e

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P R E F A C E

The present paper is the record of studies which have been carried out under the direction of Professor Dr. Junji Furukawa in 1957 -- 1961. The studies are concerned with the behavior of organometallic compound as catalyst for polymerization reaction. The writer attempted to draw a general rule for the catalytic action classifying organometallic compounds according to the catalytic nature. Some considerations were also made on characteristic reactions observed in organometallics catalyzed polymerization.

The writer wishes to express his gratitude to Professor Dr. Junji Furukawa for his constant guidance and encouragement throughout the work. He is also deeply grateful to Dr. Teiji Tsuruta for his valuable suggestions rendered during the course of the studies.

The writer also acknowledges his indebtness to Dr. Akihiro Kawasaki and Mr. Go Wasai for their kind assistance and useful advice in the measurement and analysis of X-ray diffraction pattern and infrared spectrum of polymer sample.

Furthermore, the writer is grateful to Messrs. Nariyoshi Kawabata, Norimasa Yoshida, Ryoji Sato and Yoshindo Tomoi for their active collaborations in the course of experiments.

Finally, to Miss Yōko Ōchi the writer wishes to express his indebtness for generous assistance in the typing of the manuscript.

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December, 1961.

C O N T E N T S

I N T R O D U C T I O N

Organometallic compound usually means the compound with carbon-metal bond. The word 'metal' is used in a wide sense in this paper, including all elements other than hydrogen, carbon, nitrogen, sulfur, halogen and rare gases.

The history of organometallic compounds is commonly supposed to have begun with the famous researches of Robert Bunsen on cacodyl, $(CH_3)_4As_2$, in 1841. In the early studies in this field, organozinc- and organomercury-compounds took an important part.

An epoch-making progress in organometallic chemistry was made by the discovery of Grignard reagent, which is moderately reactive to handle comparing with the other organometallics ever known, and has played very important role in both practical and fundamental fields.

One of the most brilliant accomplishment in this field is silicone industry. Besides, organolithium compound was found to show specific reactions and gave new practical utilities. Organotin compound as stabilizing agent of poly(vinyl chloride) also became important.

Even some organometallic compounds of the transition metals, e. g., titanium, were successfully prepared. A new type of compound of transition metal, ferrocene, was also discovered.

One of the prominent advances recently made in the chemistry of

organometallic compound, is that in organoaluminum compound, the industry of which was established for organic reagent and polymerization catalyst -- Ziegler catalyst.

Besides organoaluminum compound, sodium alkyl and lithium alkyl are utilized as polymerization catalysts for olefin or diolefin. Organosodium compound is known as a component of 'Alfin catalyst', which gives a stereospecific polymer of styrene. Organolithium compound has been used for the preparation of some stereospecific diene rubbers.

It was since the discovery of Ziegler catalyst ,however, that organometallic compounds have especially caught the attention of many investigators. Closely relating to this field a large number of papers and patents have appeared in the stereospecific polymerization of substituted ethylenes with complex metal catalyst. Much interest has been attendant to such polymerizations and several mechanisms have been proposed to explain the stereospecific action of the catalysts. But there has been presented no conclusive explanation as yet.

However, the attention was chiefly attracted to the field of organoaluminum compound, and no extensive work on the organometallic compounds of the other elements had been done about five years ago when the writer started to research in this field.

The writer planned an extensive work on the organometallic compounds as catalyst in vinyl polymerization, especially expecting the formation of stereospecific polymer. The nature of organometallic compound as polymerization catalyst was also studied on the basis of the periodic table, considering electronegativity of the metal.

Among the organometallic compounds, alkylboron, organocalcium compound, metal ketyl and alkylmercury were studied in some detail as the polymerization catalyst of vinyl monomers. The compounds of barium, zinc, tin, phosphor and bismuth were also studied. Including the organometallics mentioned above, the behavior of metal alkyl -- metal halide systems in vinyl polymerization were also studied, and comparison was made with 'coordinated anionic' olefin polymerization by similar systems.

SUMMARY

This paper consists of 7 chapters. Summaries of these chapters are as follows.

In Chapter 1, the behavior of alkylboron is described. Alkylboron was found to be an active catalyst for the polymerization of vinyl chloride, vinyl acetate, methacrylic esters, acrylic esters and acrylonitrile. In the alkylboron catalyzed vinyl polymerization, molecular oxygen and some oxygen-containing compounds present in the system were found to play an influential role as cocatalyst, and the binary mixtures of alkylboron and peroxides such as hydrogen peroxide or organic peroxides were found to be the most suitable catalysts for the vinyl polymerization. Copolymerization of vinyl monomers by these systems gave copolymer with a similar composition to those of usual radical copolymer. The activity of organoboron compounds with various alkyl groups was examined and the reactivity with oxygen of these compounds was found to be closely related to the catalytic activity. A radical mechanism of the polymerization reaction by intermediate alkylboron peroxide was postulated.

Chapter 2 is concerned with organocalcium compound. Calcium zinctetraethyl complex $CaZn(C_2H_5)_4$, has been found to induce the polymerization of some vinyl compounds such as styrene, methyl methacrylate and acrylonitrile. Calcium zinctetraethyl was prepared according to the

method of Gilman, starting from diethylzinc and calcium metal. Vinyl acetate and vinyl chloride were not polymerized by the complex. Oxygen, quinones and nitrobenzene suppress the polymerization. Copolymerization of methyl methacrylate and styrene by the complex gave typically anionic monomer reactivity ratios. A kinetic study on the polymerization also supported the anionic mechanism: a small value of the overall activation energy; the rate of polymerization proportional to the concentrations of monomer and catalyst; and the degree of polymerization proportional to the monomer concentration but independent of the catalyst concentration. A sample of polystyrene obtained by the catalyst has been shown to be an isotactic polymer. Poly(methyl methacrylate) formed by the catalyst was also found to be a crystalline polymer.

Chapter 3 describes the action of metal ketyl as polymerization catalyst. Some metal ketyls (mono-alkali metal complex of non-enolizable ketone) were found to induce the polymerization of vinyl compounds such as acrylonitrile and methyl methacrylate. Styrene was not polymerized by the ketyls. On the other hand, the di-alkali metal complex of the ketone had a greater activity than the ketyl. By the dimetal complex, styrene was also polymerized readily to a quantitative yield, even at low temperature. In the polymerization of styrene, the formation of living polymer was observed. A study on the copolymerization by the ketyl or the dimetal complex showed the polymerization to be anionic. Variation in the kind of ketone and metal component of the ketyl or the kind of solvent, appreciably affected the catalytic activity of the ketyl. No effect of solvent, however, was found on the copolymer composition.

Some samples of poly(methyl methacrylate) obtained by ketyl or dimetal complex were proved to have the same infrared absorption spectrum as that of the type-F crystallizable polymer. Consideration was made on the possible mechanism of the polymerization.

Chapter 4 deals with organomercury compound. Catalytic activity of di-n-butylmercury was examined and this compound alone was found to be ineffective for vinyl polymerization. On the other hand, binary systems composed of di-n-butylmercury and some metal halides were active initiators for the polymerization of vinyl acetate, methyl methacrylate, methyl acrylate and acrylonitrile. There was found a selectivity in the kind of the metal halide effective as cocatalyst in combination with the mercury alkyl. Vinyl polymerization by these binary systems was suppressed by quinone and oxygen. Vinyl copolymer obtained had a similar composition to that by the usual radical copolymerization, independently of the kind of metal halide component in the catalyst system. By the kinetic studies of the polymerization, activation energy of the reaction was proved to have the value of a similar magnitude as found in the usual radical polymerization. From these observations, the vinyl polymerization by di-n-butylmercury -- metal halide systems may be considered to proceed by a radical mechanism.

Chapter 5 describes the behavior of metal alkyl -- metal halide system in vinyl polymerization. In connection with the dibutylmercury -- metal halide system mentioned above, the behavior of various metal alkyl -- metal halide systems as vinyl polymerization catalyst were investigated. Polymerization of vinyl compound can be induced when

metal alkyl is mixed with a suitable halide in the presence of vinyl monomers. On the contrary, the binary system prepared in the absence of the monomer has much lower catalytic activity. The cocatalytic activity of metal halides depends largely upon the nature of its partner metal alkyl, though halogen compounds of metals with the electronegativity ranging from 1.5 to 2.0 are generally effective. Results of copolymerization experiments showed most of the vinyl polymerization by metal alkyl -- metal halide system to proceed according to a radical mechanism. Polymerization of glycol dimethacrylate by these catalysts resulted in gelified polymers which showed electron paramagnetic resonance absorption signals. Discussion is made on a probable mechanism of vinyl polymerization by metal alkyl -- metal halide system in connection with the coordinated anionic olefin polymerization.

Chapter 6 is concerned with miscellaneous organometallic compounds, which are not mentioned in the other chapters of this paper. The compounds of barium, zinc, tin, phosphor and bismuth are described. Organobarium compound shows a similar property to organocalcium compound. Crystallizable polymers of some monomers are obtained by the compound. Zinc- and bismuth-alkyls induce oxygen-cocatalyzed radical polymerization of vinyl monomers, though their activity is less than organoboron compound. Trialkylphosphor gives only low polymers. Tetraalkyltin is quite inactive for vinyl polymerization.

In the last chapter, the experimental results by the writer are arranged and considered according to the periodic table, together with the results so far obtained by other investigators. Six types of reactions

were found in the organometallics-catalyzed polymerization. Organometallic compounds are classified according to these reaction types into six groups (see Chapter 7, Table III). Metal alkyl, RM, can induce the anionic polymerization when the metal, M, belongs to groups I_a and II_a in the periodic table. Alkyl compounds of the other metals cannot induce vinyl polymerization by themselves, unless the C-M bond-strengths in these compounds are weak enough to break under the influence of heat or light (Hg, Pb). Most of the organometallic compounds which are sensitive to oxygen can induce oxygen-cocatalyzed radical polymerization. The compounds of Al, Zn, Cd, B, Sb and Bi are characterized by this reaction. Intermediate organometallic peroxide formed in course of the reaction with oxygen is considered to be active initiator. A wide variety of organometallic compounds are used as Ziegler type (coordinated anionic) catalyst in olefin polymerization. For the polymerization of polar vinyl monomers, however, these catalyst complexes behave as radical initiator and give non-stereospecific polymer. Some disscussions on the nature of Ziegler-Natta type catalyst were made.

C H A P T E R 1.

ORGANOBORON COMPOUND

Section 1. Introduction

Of the organometallic compounds of group III_a metals in the periodic table, alkylaluminum is well-known as one component of the Ziegler catalyst. Galium- and indium-alkyls were also reported to cause the polymerization of ethylene. However, there have been no investigations on the behavior of organoboron compound in the polymerization of olefins or polar vinyl monomers.

In their normal covalent states with valences of 3, the elements in Group III are powerful electron acceptors owing to the existence in the valence shells of unfilled orbitals that can accommodate electrons from electron donor atoms. As a result, the alkyls of the Group III elements are among the most reactive of organometallic compounds, both in the vigor of their reactions with oxidizing agents and other electron donor groups and in the wide variety of derivatives formed. The alkyls of the Group III elements have a tendency to form polymer also as a consequence of the strong electron-acceptor properties of the elements and the tendency is most marked with the lower alkyls of aluminum. Alkyls of gallium and indium are also known to be associated or polymerized

under certain conditions. This tendency may be related to the stereospecificity observed in the Ziegler-type polymerization reaction.

The alkyls of boron, however, are not associated, probably because of the small size of the boron atom relative to the surrounding organic groups.

In this connection it is interesting to examine the catalytic activity of alkylboron in vinyl polymerization.

Section 2. Experimental

2-1. Materials

a) Organoboron Compounds

Triethylboron, $B(C_2H_5)_3$, was prepared by the condensation of ethylmagnesium bromide and boron trifluoride in diethyl ether: yield, 86 %; b. p., 90 -- 97°C. (lit.[1], b. p., 95°C.). Other trialkyl and triaryl boranes were prepared similarly. The yields and the boiling points of these boranes are summarized in Table I. The procedure proposed by J. R. Johnson et al.[2] was found not to be satisfactory owing to the large susceptibility of trialkylboron to oxygen.

Di-n-butylboron oxide, $(n\text{-}C_4H_9)_2BOB(n\text{-}C_4H_9)_2$, was prepared by treating tri-n-butylboron with an aqueous solution of hydrogen bromide in the heat[2]: Yield, 29 %; b. p., 130 -- 132°C./ 10 mm. Hg (lit.[2], 136°C./ 12 mm. Hg).

Table I. Trialkyl- and Triaryl-boron

No.	Borane	Yield (%)	Boiling point (°C./mm.Hg)	Ref.
1	Tri-n-butylboron	91	90/10	2)
2	Triphenylboron	12	168/ 5	3)
3	Tribenzylboron	30	229--232/13	4)
4	Tricyclohexylboron	11	194/15	5)

n-Butyl di-n-butylboronite, $(n\text{-}C_4H_9)_2BO(n\text{-}C_4H_9)$, was obtained by distilling the reaction mixture of di-n-butylboron oxide and n-butyl alcohol[2]: Yield, 66 %; b.p. 111 -- 113°C./ 20 mm.Hg (lit.[2], b.p. 110 -- 111°C./ 19 mm.Hg or 120 -- 121°C./ 24 mm.Hg).

Di-n-butyl n-butylboronate, $(n\text{-}C_4H_9)B(O\text{-}n\text{-}C_4H_9)_2$, was obtained by the reaction of tri-n-butyl borate with n-butylmagnesium bromide[6, 7]: Yield, 4 %; b.p. 99°C./ 11 mm.Hg (lit.[6], b.p. 105°C./ 10 mm.Hg).

Tri-n-butyl borate, $B(O\text{-}n\text{-}C_4H_9)_3$, was prepared by heating boron trioxide and n-butyl alcohol[8]: Yield, 69 %; b.p. 114°C./ 14 mm.Hg (lit.[8], b.p. 115°C./ 15 mm.Hg).

Di-n-butylboron bromide, $(n\text{-}C_4H_9)_2BBr$, was obtained by the reaction of tri-n-butylboron with bromine[2]: Yield, 45 %; b.p. 90 -- 93°C./ 25 mm.Hg (lit.[2], b.p. 88 -- 90°C./ 23 mm.Hg).

Di-n-butylboron chloride, $(n\text{-}C_4H_9)_2BCl$, was prepared by passing dry hydrogen chloride through tri-n-butylboron at 110°C.[9]: Yield, 73 %; b.p. 54 -- 56°C./ 9.5 mm.Hg (lit.[9], b.p. 47 -- 48°C./ 7 mm.Hg).

Tri-n-butylboroxine, $(n\text{-}C_4H_9BO)_3$, was prepared by heating tri-n-

butylboron with boron trioxide under total reflux[10]: Yield, 3.1 %; b.p. 132 -- 134°C./ 15 mm.Hg (lit.[10], b.p. 134°C./ 16 mm.Hg).

b) Monomers and Solvents

Vinyl acetate[11] was washed five times with a saturated solution of sodium bisulfite and five times with water, dried over anhydrous potassium carbonate, and was distilled. A fraction boiling at 72.5 -- 73°C. was distilled with the addition of a small quantity of benzoyl peroxide under nitrogen immediately before use. Methyl methacrylate was steam-distilled twice, dried with calcium chloride, and was distilled under reduced pressure. Styrene[12] was washed successively with 10 % solution of sodium hydroxide, with water, and was steam-distilled. Distilled styrene was dried on calcium chloride and was distilled again under reduced pressure (b.p. 55°C./ 33 mm.Hg). A distillation was repeated in vacuo immediately before use. Acrylonitrile[13] was washed successively with 5 % sulfuric acid and with 5 % caustic soda, dried on calcium chloride and was rectified (b.p. 77°C.). n-Butyl vinyl ether was washed by potassium hydroxide solution (pH 7.5 -- 8.0) several times, dried over potassium hydroxide beads and distilled; b.p. 94°C. Vinyl chloride of commercial material was used without further purification. n-Hexane[14] was washed with sulfuric acid, dried with calcium chloride, and was distilled. The distillate was dried over metallic sodium. Manganese dioxide was prepared by the reaction of potassium permanganate with glucose in a weak alkaline solution. All other organic and in-

organic reagents were of chemical pure grade and were used without further purification.

2-2. Polymerization

In most cases, polymerizations were carried out in sealed tubes or glass stoppered test tubes kept standing or rotating in a constant temperature bath. In some cases methanol or n-hexane was added to a reaction system as a solvent for catalyst. After a definite time interval, the polymerization was stopped by adding methanolic ammonia in amount of 120 mole percent with respect to the organoboron compound used.

2-3. Separation and Purification of Polymer

Polyvinyl acetate was precipitated by successive addition of petroleum ether and water to the reaction mixture. The other polymers were precipitated by adding methanol to the reaction mixture. After removing the solvents and inorganics by treating with boiling water, the polymer was collected and dried to a constant weight at 45 -- 50°C. Copolymers of styrene and methyl methacrylate, and of styrene and vinyl acetate were worked up in a similar way. When metal oxides were used as co-catalyst, the polymer formed was dissolved in acetone and separated from the metal oxide by means of centrifugation (10,000 r.p.m.).

2-4. Deacetylation of Polyvinyl Acetate

To a solution of 10 g. polyvinyl acetate in 100 ml. methanol was added 30 % caustic soda solution (1/3 equivalent to the polymer) at 50°C. under stirring. After kept standing at 60°C. for an hour, polyvinyl alcohol was separated, immersed in methanol, and was dried in vacuo at room temperature. The dried polyvinyl alcohol was dissolved again in water and was treated with aqueous sodium hydroxide*) at 30 -- 35°C. to remove residual acetyl groups. Methanol was added to the solution and the precipitated polyvinyl alcohol was worked up as stated above.

2-5. Molecular Weight Measurement

The molecular weights of the polymers were determined viscometrically by the use of the equations in Table II.

Table II. Viscosity Equations used ($[\eta] = KM^{\alpha}$)

No.	Polymer	Solvent	Temp. (°C.)	$K \cdot 10^4$	α	Ref.
1	Polymethyl methacrylate	Acetone	25	0.96	0.96	15)
2	Polyacrylonitrile	Dimethylformamide	25	1.66	0.81	16)
3	Polystyrene	Toluene	30	1.2	0.70	17)
4	Polystyrene	Toluene	30	0.55	0.81	17)
5	Polyvinyl acetate	Acetone	30	5.02	0.62	18)
6	Polyvinyl alcohol	Water	30	6.66	0.64	19)

*) The concentration was equivalent to 3 % of the acetyl group of polyvinyl acetate used.

Section 3. Triethylboron as Initiator for Vinyl Polymerization

Triethylboron has been found to initiate the polymerization of some vinyl compounds such as vinyl acetate, vinyl chloride, methacrylic esters, acrylic esters and acrylonitrile.

To a solution of 5 ml. (0.032 mole) of vinyl acetate in 15 ml. of n-hexane was added 0.66 ml. (0.0047 mole) of triethylboron. The solution became turbid immediately owing to the formation of the fine dispersion of poly(vinyl acetate). The reaction temperature was controlled at 20°C. by removing the heat evolved in the course of polymerization.

After two hours, water was added to the mixture and air was slowly introduced to decompose the catalyst. The polymer was separated from monomer and solvent by steam distillation, and was dried at 55°C. The conversion was 42 %, and viscosity average molecular weight of the polymer was 1.9×10^4.

Similar results were obtained from experiments with the other vinyl compounds. These are summarized in Table III.

Triethylboron causes the vinyl monomers, e. g., vinyl chloride, to polymerize at moderate rate even at temperature as low as -30°C., which may make possible the production of polymers with regular head-to-tail structure or with no side chains. In fact, poly(vinyl chloride) with higher stereoregularity than the conventional polymer was obtained by catalyst systems of trialkylboron in admixture with some organic hydroperoxides.[31)]

Table III. Vinyl Polymerization using Triethylboron as Initiator

Monomer		Catalyst/monomer	Reaction temp., (°C.)	Conversion, (%)	M.W. $\times 10^{-4}$
Name	Mole	(mole ratio)			
Acrylonitrile	0.076	0.062	20	77	1.8
Methyl methacrylate	0.047	0.100	20	55	5.2
Vinyl chloride	1.000	0.021	-30	10	5.3
Vinyl acetate	0.052	0.091	20	42	1.9
Styrene	0.044	0.108	20	0	---
n-Butyl vinyl ether	0.039	0.121	20	0	---

Since triethylboron is not decomposed with water, quite differently from the other alkyls of the Group III elements, suspension polymerizations in water are also possible with the boron compound as initiator.

Section 4. Effect of Molecular Oxygen and Oxygen-containing Compounds on Trialkylboron-catalyzed polymerization

There was found a remarkable co-catalytic action of oxygen and oxygen compounds in this polymerization. Recently, Kolesnikov and Fedorova described[20] that acrylonitrile was not polymerized by tributylboron in the system where the trace of molecular oxygen was completely excluded. The writer have carried out a series of experiments in more detail.

Table IV. Effect of Oxygen upon Polymerizations of Vinyl Acetate and of Styrene

A. Vinyl acetate[a)]

No.	O_2/ $B(C_2H_5)_3$ (Mole ratio × 10^2)	Conversion (%)	Average degree of polymerization $\bar{P}_{PVAc} \times 10^{-2}$
1	1.6	8.3	5.1
2	3.2	10.7	5.3
3	6.4	16.6	4.2
4	9.5	22.9	4.1
5	14.3	40.4	3.3

B. Styrene[b)]

No.	Gas phase (35 cc.)	Conversion (%)	$\bar{P}_{PSt}$
1	Air	9.4	293
2	Nitrogen	Very small	---
3	Air	20.3	276
4	Nitrogen	Very small	---

a) Experimental conditions: Vinyl acetate, 0.107 mole (10 cc.); $B(C_2H_5)_3$, 2.7×10^{-3} mole; temp., 30°C.; time, 26 hrs.; under standing.

b) Experimental conditions: Styrene, 0.0872 mole (10 cc.); $B(n\text{-}C_4H_9)_3$, 1.74×10^{-3} mole; temp., 60°C.; time, 3 hrs.; under standing.

4-1. Effect of Oxygen

The effect of oxygen on the polymerization of vinyl acetate and of styrene is shown in Table IV. It is seen from the table that oxygen has a marked effect on the polymerization.

In the vinyl acetate polymerization under various partial pressures of oxygen, it was found that the larger the partial pressure of oxygen, the larger was the rate of oxygen absorption as well as the rate of polymerization. The result is shown in Table V.

These reactions were carried out in test tubes being kept standing, where the polymerization was observed to start on the contact surface with the gas phase. If the experiment was carried out under vigorous shaking,

Table V. Vinyl Acetate Polymerization under Various Partial Pressure of Oxygen[a)]

No.	Volume percent of oxygen (%)[b)]	Volume of absorbed oxygen (cc.)	Conversion (%)
1	Less than 0.1	0.4	44.4
2	5	1.0	48.8
3	10	1.8	55.0
4	20	2.5	57.8
5	50	Unmeasurable[c)]	----

a) Experimental conditions: Vinyl acetate, 0.107 mole; $B(n\text{-}C_4H_9)_3$, 1.07×10^{-3} mole; temp., 30°C.; time, 2 hrs.; under standing.

b) Values in gas phase (53 cc.).

c) Explosive polymerization.

there was isolated no polymer. These results seem to suggest that molecular oxygen may react with the boron compound to produce an active radical which induces the polymerization; but excess oxygen does terminate the radical chain in the same manner as in the usual radical polymerization.

4-2. Effect of Hydrogen Peroxide

The effect of hydrogen peroxide upon the polymerization of various vinyl monomers is shown in Table VI. In Table VII the effect of the molar ratio of triethylboron to hydrogen peroxide on the conversion of vinyl acetate is shown.

The conversion increases with increasing quantity of hydrogen peroxide up to 80 mole-% with respect to triethylboron, but beyond this limit, the conversion decreases rapidly. The boron compound is probably further oxidized in part to inactive species by the excess of hydrogen peroxide. Atomic or molecular oxygen arising from hydrogen peroxide may also interfere the polymerization. From the foregoing results, the active catalysts inducing the polymerization are supposed to be "reaction product" between the trialkylboron and oxygen compounds. In order to obtain an information on the life-time of this catalyst, vinyl acetate was polymerized by various catalytic systems differing among themselves in the time of reaction between trialkylboron and hydrogen peroxide. The result is shown in Table VIII. It can be seen from Table VIII that the longer the time of reaction between the boron compound and

Table VI. Effect of Hydrogen Peroxide upon Triethylboron-initiated Polymerization of Vinyl Monomers

No.	Monomer[a]	$B(C_2H_5)_3$/Monomer (mole ratio$\times 10^2$)	$H_2O_2/B(C_2H_5)_3$ (mole ratio$\times 10^2$)	Conversion (%)
1·1	Vinyl acetate[b] (0.104 mole)	2.6	80	66.0
1·2	" "	2.6	60	32.3
1·3	" "	2.6	40	24.4
1·4	" "	2.6	0	19.8
2·1	Styrene[c] (0.044 mole)	10.8	80	15.3
2·2	" "	10.8	60	11.2
2·3	" "	10.8	40	8.5
2·4	" "	10.8	0	6.7
3·1	Methyl methacrylate[d] (0.047 mole)	10.0	60	47.4
3·2	" "	10.0	40	9.2
3·3	" "	10.0	20	7.1
3·4	" "	10.0	0	5.6
4·1	Acrylonitrile[d] (0.076 mole)	6.2	60	15.1
4·2	" "	6.2	40	10.0
4·3	" "	6.2	20	6.2
4·4	" "	6.2	0	4.2

a) These monomers are not polymerized by hydrogen peroxide alone under these conditions.

b) Temp., 23°C.; time, 22 hrs.; under rotation in nitrogen.

c) Temp., 60°C.; time, 6 hrs.; under rotation in nitrogen.

d) Temp., 25°C.; time, 2 hrs.; under rotation in nitrogen.

Table VII. Effect of Hydrogen Peroxide upon Vinyl Acetate Polymerization[a)]

No.	$H_2O_2/B(C_2H_5)_3$ (mole ratio$\times 10^2$)	Conversion (%)
1	50	28.7
2	75	42.6
3	100	9.9
4	125	7.5
5	150	3.6
6	200	4.2
7	300	5.6

Table VIII. Effect of the Reaction time of Tri-n-butylboron with Hydrogen Peroxide upon Vinyl Acetate Polymerization[b)]

No.	Reaction time (min.)	Conversion (%)
1	0	62.7
2	1	57.0
3	3	42.7
4	5	25.5
5	10	16.2

a) Experimental conditions: Vinyl acetate, 0.107 mole; methanol, 1 cc.; $B(C_2H_5)_3$, 2.78×10^{-3} mole; temp., 0°C.; time, 72 hrs.; under standing in nitrogen.

b) Experimental conditions: Vinyl acetate, 0.107 mole; $B(n\text{-}C_4H_9)_3$, 1.07×10^{-3} mole; H_2O_2, 5.4×10^{-4} mole; temp., 10°C.; time, 20 hrs.; under standing in nitrogen.

the peroxide, the smaller the conversion to the polymer becomes. This result may make it possible to assume that the active species for the polymerization is of a very short life-time which is formed transiently in the reaction between trialkylboron and oxygen compounds. Thus it seems necessary for the polymerization to be induced that the boron compound was brought into reaction with an oxygen compound in the presence

of a monomer.

In Table IX, the results of examinations on the behavior of hydroquinone toward the polymerization are listed. Inhibiting action of hydroquinone seems not so significant as in the usual radical polymerization.

Table IX. Effect of Hydroquinone upon Vinyl Acetate Polymerization[a)]

No.	HO-C$_6$H$_4$-OH : H_2O_2 : $B(C_2H_5)_3$ (mole ratio)	Conversion (%)
1	0 : 8 : 10	91.3
2	4 : 8 : 10	72.7
3	8 : 8 : 10	52.7

a) The same experimental conditions as in Table VII.

4-3. Effect of Organic Hydroperoxide and Metal Oxide

Cumene hydroperoxide or tert.-butyl hydroperoxide exhibits a marked catalytic activity toward the polymerization in the presence of trialkylboron as shown in Table X.

Some metal oxides such as manganese dioxide or vanadium pentoxide were found to have co-catalytic activity toward the vinyl polymerization catalyzed by trialkylboron under nitrogen. In this polymerization, the metal oxides were gradually covered with the swollen polymer and the changes in color of the oxides were observed as the reaction time elapsed. These facts may suggest that the polymerization takes place on the surface of metal oxide. The effects of various metal oxides upon the vinyl

Table X. Vinyl Acetate Polymerization by Binary System of Tri-n-butylboron and Cumene Hydroperoxide (CHP)[a)]

CHP/B(n-C_4H_9)$_3$ (mole ratio)	Temp. (°C.)	Conversion (%)	$\bar{P}_{PVAc} \times 10^{-2}$
0.1	-40	10.9	4.5
0.1	0	16.5	4.7
0.1	40	24.6	5.5
0.1	-60	11.5	3.7
0.2	-60	14.6	3.1
0.4	-60	20.7	2.1
0.8	-60	21.0	1.9

a) Experimental conditions: Vinyl acetate, 0.107 mole; B(n-C_4H_9)$_3$, 0.107×10^{-2} mole; time, 4 hrs.; under standing in nitrogen.

polymerization are listed in Table XI. In general it can be said that the higher-order oxide of transition metals have considerable activity, in opposition to the halides and the oxyhalides.

Results of more detailed examinations on the effect of manganese dioxide are shown in Table XII. Table XII shows that the conversion increases with increasing quantity of the oxide added. With manganese dioxide in a fixed quantity, the conversion remains unchanged irrespective of changes in the quantity of the boron alkyl added. Molecular weight of the polymer was found to decrease with increasing quantity of boron alkyl as well as manganese dioxide. Figures 1 and 2 are the plots of the conversion and of the reciprocal degree of polymerization against the quantity of manganese dioxide, respectively.

Table XI. Effect of Metal Oxides upon the Polymerization of some Vinyl Monomers[a)]

No.	Monomer	Metal oxide	Gas phase	Conversion(%)	$\bar{P}\times10^{-2}$
1·1	Vinyl acetate[b)]	MnO_2	N_2	23.0	15.1
1·2	"	V_2O_5	N_2	23.2	19.5
1·3	"	CuO	N_2	13.8	6.5
1·4	"	WO_3	N_2	13.0	----
1·5	"	H_2WO_4	N_2	5.8	----
1·6	"	$TiCl_3$	N_2	----	----
1·7	"	$VOCl_3$	N_2	----	----
1·8	"	----	N_2	4.4	13.4
1·9	"	----	Air	15.7	10.1
2·1	Styrene[c)]	MnO_2	N_2	37.4	----
2·2	"	V_2O_5	N_2	28.2	----
2·3	"	WO_3	N_2	16.5	----
2·4	"	----	N_2	7.5	----
2·5	Styrene[d)]	MnO_2	N_2	7.78	----
2·6	"	V_2O_5	N_2	6.55	----
2·7	"	CoO	N_2	6.13	----
2·8	"	WO_3	N_2	6.86	----
2·9	"	----	N_2	5.86	----
2·10	"	----	Air	13.0	----
3·1	Methyl methacrylate[e)]	MnO_2	N_2	34.8	----
3·2	"	V_2O_5	N_2	13.0	----
3·3	"	CuO	N_2	14.7	----
3·4	"	WO_3	N_2	28.2	----
3·5	"	----	N_2	11.5	----
3·6	"	----	Air	65.5	----
4·1	Acrylonitrile[f)]	MnO_2	N_2	6.2	6.91
4·2	"	V_2O_5	N_2	20.0	8.57
4·3	"	CuO	N_2	18.1	8.42
4·4	"	----	N_2	1.8	----

a) All the polymerizations were carried out under rotation.
b) Experimental conditions: 1.3 mole % $B(C_2H_5)_3$ for monomer; 50 mole % metal oxide for $B(C_2H_5)_3$; temp., 25°C.; time, 72 hrs.
c) Experimental conditions: 10.8 mole % $B(C_2H_5)_3$ for monomer; 25 mole % metal oxide for $B(C_2H_5)_3$; temp., 25°C.; time, 32 hrs.
d) Experimental conditions: 10.8 mole % $B(C_2H_5)_3$ for monomer; 25 mole % metal oxide for $B(C_2H_5)_3$; temp., 60°C.; time, 3 hrs.
e) Experimental conditions: 10 mole % $B(C_2H_5)_3$ for monomer; 25 mole % metal oxide for $B(C_2H_5)_3$; temp., 25°C.; time, 2 hrs.
f) Experimental conditions: 10 mole % $B(C_2H_5)_3$ for monomer; 25 mole % metal oxide for $B(C_2H_5)_3$; temp., 25°C.; time, 19 hrs.

Table XII. Effect of the Mole Ratio of MnO_2 to BR_3 upon Vinyl Acetate Polymerization

No.	MnO_2/BR_3 (mole ratio)		Conversion (%)	$\bar{P}x10^{-2}$	No.	MnO_2/BR_3 (mole ratio)		Conversion (%)	$\bar{P}x10^{-2}$
A.	With MnO_2 in a constant quantity				B.	With BR_3 in a constant quantity			
1·1	8	a)	38.1	23.9	3·1	0.25	c)	8.8	12.3
1·2	4	a)	54.9	10.6	3·2	0.5	c)	31.7	7.8
1·3	2	a)	54.8	7.9	3·3	1.0	c)	52.8	5.3
1·4	1	a)	56.2	5.9	3·4	2.0	c)	81.8	4.2
1·5	0.5	a)	50.0	4.3	4·1	0.25	d)	2.8	10.6
2·1	4	b)	32.2	18.1	4·2	0.5	d)	8.1	11.1
2·2	2	b)	34.6	16.7	4·3	1.0	d)	21.4	10.4
2·3	1	b)	37.2	12.5	4·4	2.0	d)	47.5	8.4
2·4	0.5	b)	38.5	8.0	4·5	3.0	d)	78.4	5.9
2·5	0.25	b)	37.9	4.3	4·6	4.0	d)	90	5.0

a) Experimental conditions: Triethylboron as initiator; vinyl acetate, 0.214 mole; MnO_2, 2.81×10^{-3} mole; temp., 60°C.; time, 3 hrs.; under rotation in nitrogen.

b) Experimental conditions: Tri-n-butylboron as initiator; vinyl acetate, 0.107 mole; MnO_2, 1.07×10^{-3} mole; temp., 60°C.; time, 3 hrs.; under rotation in nitrogen.

c) Experimental conditions: Triethylboron as initiator; vinyl acetate, 0.214 mole; $B(C_2H_5)_3$, 2.81×10^{-3} mole; temp., 60°C.; time, 3 hrs.; under rotation in nitrogen.

d) Experimental conditions: Tri-n-butylboron as initiator; vinyl acetate, 0.107 mole; $B(n\text{-}C_4H_9)_3$, 1.6×10^{-3} mole; temp., 60°C.; time, 3 hrs.; under rotation in nitrogen.

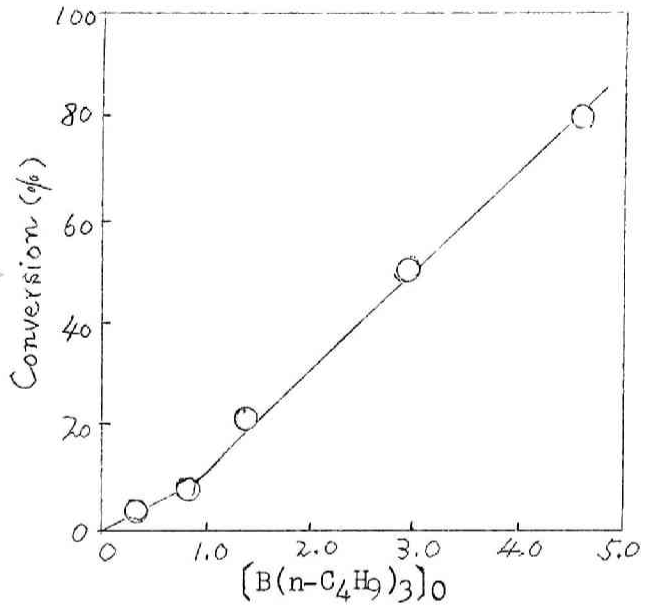


Fig. 1. Relationship between the conversion and the initial concentration of tri-n-butylboron, $[B(n\text{-}C_4H_9)_3]_0$.

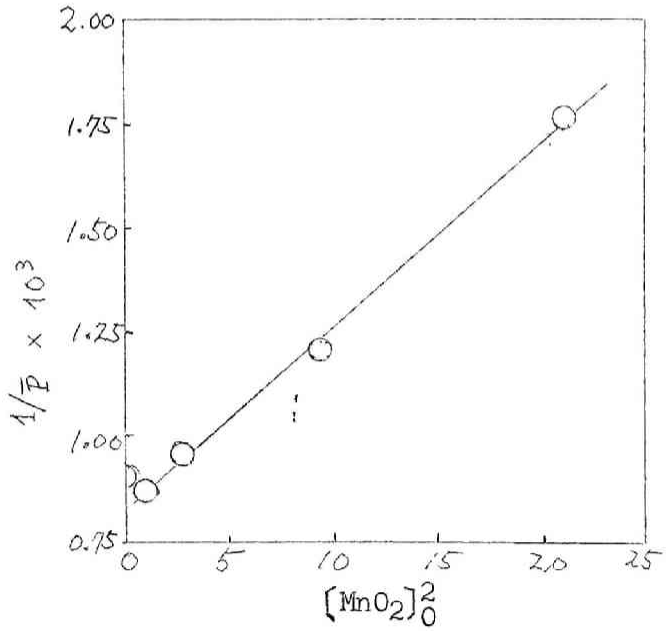


Fig. 2. Plots of the reciprocal of the average degree of polymerization against the square of the initial concentration of manganese dioxide, $[MnO_2]_0^2$.

Section 5. Polymerizations with Alkylboron Derivatives

As described above, molecular oxygen and oxygen compounds exhibit co-catalytic activity toward the vinyl polymerization catalyzed by trialkylboron. On the other hand, it has long been known that, in the reaction of trialkylboron with oxygen compounds, various oxidized compounds, such as R_2BOR, $RB(OR)_2$ and $B(OR)_3$, are obtainable according to reaction conditions.[21] We examined on the activities of these oxidized products toward the polymerization of vinyl acetate*). For comparison, the behavior of di-n-butylboron halide was also examined. The results are summarized in Table XIII.

Table XIII. Vinyl Acetate Polymerization with Tri-n-butylboron derivatives[a]

No.	Tri-n-butylboron derivative	Conversion (%) In air	Conversion (%) In nitrogen
1	$B(n\text{-}C_4H_9)_3$	70.0	7.7
2	$(n\text{-}C_4H_9)_2BOB(n\text{-}C_4H_9)_2$[b]	92.3	20.6
3	$(n\text{-}C_4H_9)_2B(O\text{-}n\text{-}C_4H_9)$	75.2	1.5
4	$(n\text{-}C_4H_9)B(O\text{-}n\text{-}C_4H_9)_2$	0	0
5	$B(O\text{-}n\text{-}C_4H_9)_3$	0	0
6	$(n\text{-}C_4H_9BO)_3$	0	0
7	$(n\text{-}C_4H_9)_2BBr$	58.8	Very small
8	$(n\text{-}C_4H_9)_2BCl$	11.9	Very small

a) Experimental conditions: Vinyl acetate, 0.107 mole; the boron compound used are 1 mole % with respect to the monomer. Temp., 20°C.; time, 20 hrs.; under standing.
b) 1/2 Mole % with respect to the monomer.

*) The polymerization of various vinyl compounds except for vinyl acetate was studied by Ashikari[22].

These oxidized compounds, except for $n\text{-}C_4H_9B(O\text{-}n\text{-}C_4H_9)_2$, $B(O\text{-}n\text{-}C_4H_9)_3$ and $(n\text{-}C_4H_9BO)_3$, were found to exhibit catalytic activities which decrease in the order:

$$(n\text{-}C_4H_9)_2BOB(n\text{-}C_4H_9)_2 > B(n\text{-}C_4H_9)_3 > (n\text{-}C_4H_9)_2B(O\text{-}n\text{-}C_4H_9) > (n\text{-}C_4H_9)_2BBr > (n\text{-}C_4H_9)_2BCl$$

It is to be noted that, in these cases too, oxygen exerted a remarkable co-catalytic action, as seen in Table XIII. From the result obtained above, it may be concluded that a compound which combines more easily with oxygen has a greater catalytic action.

Triphenylboron, which was not inflammable in air, was found to have much smaller activity compared with the aliphatic boron derivatives. In Table XIV, the catalytic activities of triphenyl-, tribenzyl-, and tricyclohexylboron are compared.

The prominent catalytic activity of tricyclohexylboron seems to suggest that the decrease of activity in triphenylboron is not ascribed to the steric hindrance of the phenyl group because cyclohexyl group is considered to have much the same bulkiness. Thus, we feel the lowering of the reactivity in triphenylboron to be better interpreted in terms of the resonance stabilization to which the 2p- and π-orbitals of boron and phenyl group may contribute, respectively.

Tribenzylboron, on the other hand, exhibits the significant activity, the conjugation between phenyl and boron being interrupted with the methylene groups.

Table XIV. Triphenyl-, Tribenzyl- and Tricyclohexylboron-initiated Polymerization of Vinyl Monomers

No.	Catalyst	Monomer	Gas phase	Conversion (%)	$\bar{P}\times10^{-2}$
1·1	Triphenylboron[a)]	Styrene	Air	0	----
1·2	"	Styrene	N_2	0	----
1·3	"	Methyl methacrylate	Air	2.2	----
1·4	"	Methyl methacrylate	N_2	5.9	----
1·5	"	Acrylonitrile	Air	Very small	----
1·6	"	Acrylonitrile	N_2	Very small	----
1·7	"	Vinyl acetate	Air	0	----
1·8	"	Vinyl acetate	N_2	0	----
2·1	Tribenzylboron[b)]	Styrene	Air	14	3.3
2·2	"	Styrene	N_2	10	4.3
2·3	"	Methyl methacrylate	Air	92	21.0
2·4	"	Methyl methacrylate	N_2	16	22.3
2·5	"	Acrylonitrile	Air	----[d)]	----
2·6	"	Acrylonitrile	N_2	27	12.9
2·7	"	Vinyl acetate	Air	31	3.4
2·8	"	Vinyl acetate	N_2	0	----
3·1	Tricyclohexylboron[c)]	Methyl methacrylate	Air	100	15.1
3·2	"	Methyl methacrylate	N_2	100	29.0
3·3	"	Vinyl acetate	Air	56	16.4
3·4	"	Vinyl acetate	N_2	55	18.1

a) Experimental conditions: Monomer, 0.1 mole; triphenylboron, 5 mole % for monomer; temp., 20°C.; time, 21 hrs.

b) Experimental conditions: Monomer, 0.1 mole; tribenzylboron, 1 mole % for monomer; temp., 10°C.; time, 19 hrs.

c) Experimental conditions: Monomer, 0.1 mole; tricyclohexylboron, 1 mole % for monomer; temp., 10°C.; time, 19 hrs.

d) Explosive polymerization.

Section 6. Copolymerization

In order to examine the mechanism of the present polymerization, the copolymerizations of styrene-methyl methacrylate and of styrene-vinyl acetate were studied with tributylboron as catalyst. Taking styrene as monomer (1), monomer reactivity ratios ($r_1 = 0.49$; $r_2 = 0.41$) were calculated from the data in Table XV according to the Mayo-Lewis equation[23].

Table XV. Copolymerization of Styrene and Methyl Methacrylate[a]

No.	Mole fraction of styrene in monomer mixture	Oxygen content of the copolymer			Mole fraction of styrene in copolymer
		from CH-analysis (%)	from O-analysis (%)	Average (%)	
1	1.0	---	---	---	---
2	0.9	5.08	5.16	5.12	0.84
3	0.8	8.38	8.23	8.31	0.74
4	0.7	10.78	10.83	10.81	0.66
5	0.6	12.81	12.97	12.89	0.60
6	0.5	15.37	15.65	15.51	0.52
7	0.4	17.21	17.22	17.22	0.46
8	0.3	19.87	19.94	19.91	0.38
9	0.2	22.15	22.05	22.10	0.31
10	0.1	25.81	26.03	25.92	0.19
11	0	---	---	---	---

a) Experimental conditions: Monomers, 0.04 mole; 4.0×10^{-4} mole $B(C_2H_5)_3$ was used as 20 % n-hexane solution; temp., 60°C.; time, 1 hr.; under rotation in nitrogen.

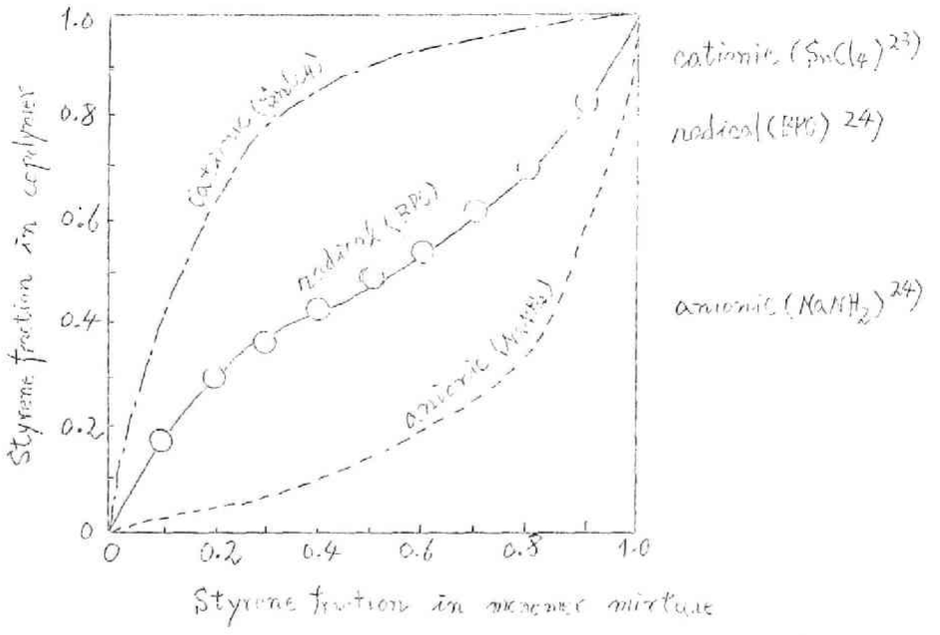


Fig. 3. Copolymer composition curves for styrene-methyl methacrylate system
○ : Triethylboron-catalyzed copolymerization

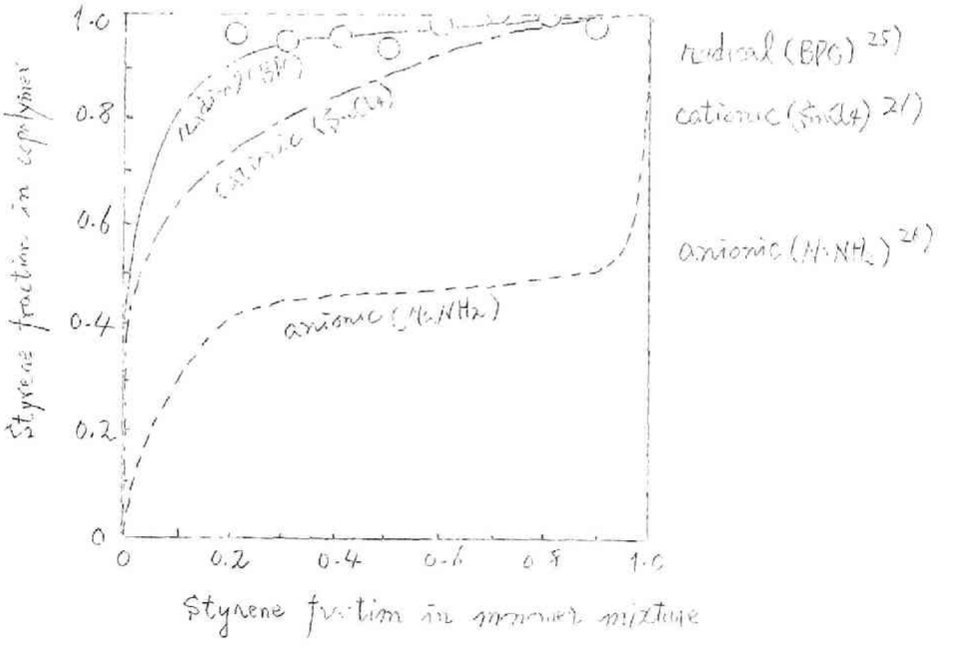


Fig. 4. Copolymer composition curves for styrene-vinyl acetate system
○ : Triethylboron-catalyzed copolymerization

These values are in good accord with those ($r_1 = 0.52 \pm 0.026$, $r_2 = 0.460 \pm 0.026$)[23] from the copolymerization induced by benzoyl peroxide. Figure 3 shows that a plot for the tributylboron-catalyzed copolymerization falls on the curved line for the typical radical copolymerization. For comparison, curves for anionic and cationic copolymerizations are also illustrated in Figure 3. From the above results,

Table XVI. Copolymerization of Styrene and Vinyl Acetate[a)]

No.	Mole fraction of styrene in monomer mixture	Oxygen content of the copolymer from CH-analysis (%)	Mole fraction of styrene in copolymer
1	1.0	----	----
2	0.9	0.22	0.99
3	0.8	0.08	1.00
4	0.7	0.10	1.00
5	0.6	0.18	0.99
6	0.5	0.94	0.97
7	0.4	0.50	0.98
8	0.3	1.10	0.97
9	0.2	0.96	0.97
10	0.1	----	----
11	0	----	----

a) Experimental conditions: Monomers, 0.04 mole; 4.0×10^{-4} mole $B(C_2H_5)_3$ was used as 20 % n-hexane solution; temp., 60°C.; time, 1 hr.; under rotation in nitrogen.

the propagation stage of the trialkylboron-catalyzed polymerization is considered to proceed according to a radical mechanism. The data of copolymerization between styrene and vinyl acetate also support the above conclusion (Table XVI, Figure 4).

Section 7. Characteristics of the Alkylboron-Catalyzed Polymerization of Vinyl Acetate

The result of the bulk polymerization of vinyl acetate catalyzed by the binary system of tri-n-butylboron-manganese dioxide is shown in Table XVII.

Table XVII. Vinyl Acetate Polymerization by Binary System $B(n\text{-}C_4H_9)_3$--MnO_2 [a)]

No.	Conversion (%)	Average degree of polymerization $\bar{P}_{PVAc} \times 10^{-3}$	$\bar{P}_{PVA} \times 10^{-3}$
1	19.3	1.08	1.22
2	28.1	1.12	1.13
3	42.8	1.27	1.24
4	69.7	1.29	1.20

a) Experimental conditions: Vinyl acetate, 0.107 mole; $B(n\text{-}C_4H_9)_3$, 1.07×10^{-3} mole; MnO_2, 1.07×10^{-3} mole; temp., 60°C.; under rotation in nitrogen.

There can be seen little difference in the degree of polymerization between polyvinyl acetate and the corresponding polyvinyl alcohol, which is in contrast to cases for the usual vinyl acetate polymerization.

A linear relationship (1) is obtainable between the reciprocal degree of polymerization and the initial concentration of trialkylboron, as shown in Table XII A and Figure 5*).

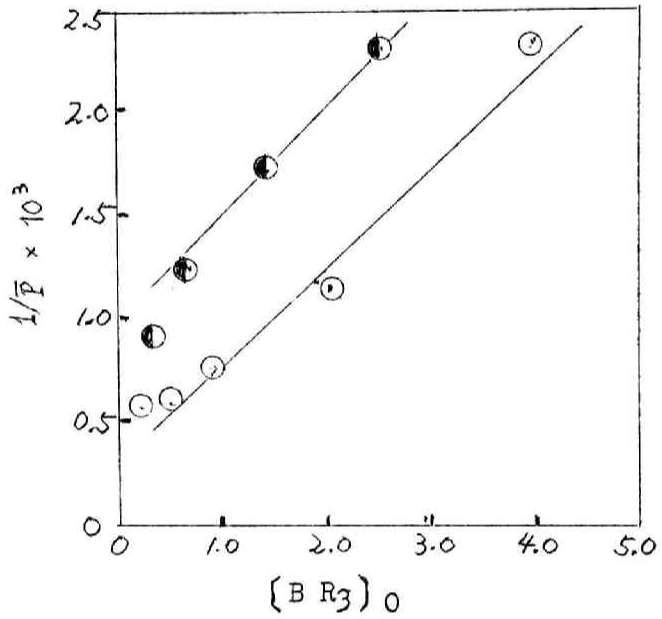


Fig. 5. Plots of the reciprocal of the average degree of polymerization against the initial concentration of trialkylboron: ○, Tri-n-butylboron-catalyzed polymerization; ◐, Triethylboron-catalyzed polymerization.

*) The difference in the values of two intercepts in Fig. 5 is due to the differences in quantity of the monomer and manganese dioxide used.

$$\frac{1}{\overline{P}_{PVAc}} = C \cdot \frac{[BR_3]_0}{[VAc]_0} + A \qquad (1)$$

where $C = 48\frac{5}{8} \times 10^{-4}$; $(BR_3)_0$, the initial concentration of triethylboron or tri-n-butylboron; $(VAc)_0$, the initial concentration of vinyl acetate. This result suggests the boron alkyl to play an important role in the chain transfer as well as the chain termination in the vinyl acetate polymerization. If the chain transfer to the boron compound predominates over the monomer transfer, there will be formed polyvinyl acetate having few side chain which is hydrolyzed to give polyvinyl alcohol of the same degree of polymerization.

The results of polymerization with chloroform as a chain transfer agent are listed in Table XVIII, where we can see again much the same degree of polymerization with respect to polyvinyl acetate and the corresponding alcohol.

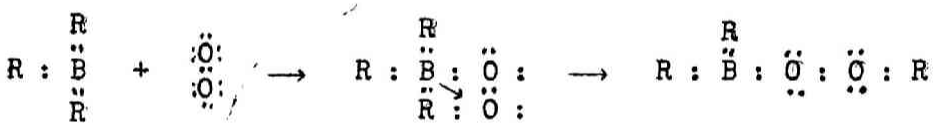
Table XVIII. Vinyl Acetate Polymerization induced by 2,2'-Azo-bis-isobutyronitrile in the Presence of Chloroform[a)]

No.	$CHCl_3$/vinyl acetate (mole ratio$\times 10^2$)	Time (hrs.)	Conversion (%)	$\overline{P}_{PVAc} \times 10^{-2}$	$\overline{P}_{PVA} \times 10^{-2}$
1	8	3	64.9	5.6	5.8
2	5	2	68.0	8.8	9.3
3	4	2.5	80.0	10.8	10.9

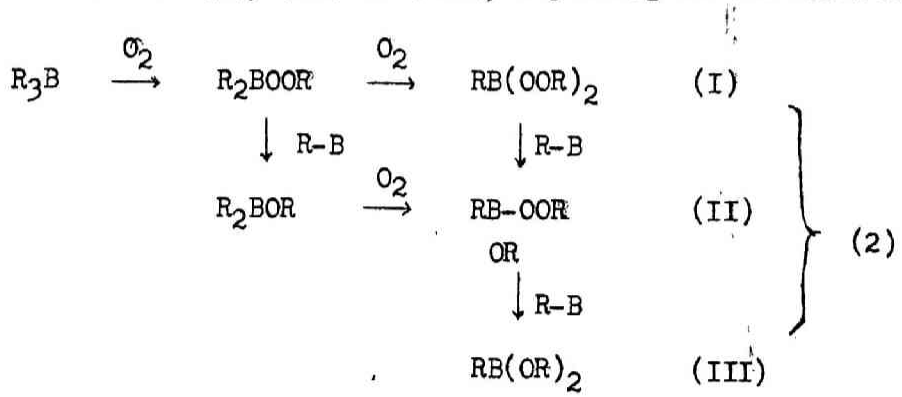
a) Experimental conditions: Vinyl acetate, 0.107 mole; 2,2'-azo-bis-isobutyronitrile, 5.35×10^{-5} mole; temp., 60°C.; under rotation in nitrogen.

Section 8. Reaction Mechanism

From the results described above, it is supposed that species playing an important role in inducing the polymerization may be an unstable product which is formed transiently in an intermediate stage to one of the oxidized compounds mentioned in the previous section. Di-n-butyl n-butylboronate, tri-n-butyl borate and tri-n-butylboroxine, which are stable in air, have no catalytic action. Parsons[27] and Petry[28] reported the existence of a peroxide in the process of oxidation of trimethylboron and inferred the process as follows:



Abraham and Davies[29] recently demonstrated that oxidation of R_3B gave initially R_2BOOR which could be reduced by an R-B group giving R_2BOR, or could be further oxidized by oxygen to $RB(OOR)_2$ and the final products might therefore be (I), (II) or (III), depending on the conditions.



From oxidation products of tri-tert-butylboron, boron oxide corresponding to (I) was isolated and identified by them. Nakayama[30] examined

the catalytic reactivity of the oxidation products of tri-n-butylboron. According to his experiment, unstable peroxide (I) is considered to be the active species of this catalyst system. From the experimental results boron peroxide prepared by the oxidation at low temperature was proved to exhibit a remarkable catalytic reactivity on the polymerization of vinyl monomers at room temperature. On the other hand, it was surprising that boron peroxide prepared by the oxidation at room temperature showed only a very weak catalytic reactivity on the polymerization, though the same content in peroxide was proved by titration. These two types of peroxide may correspond to the compounds (I) and (II) in equation (2). In the foregoing sections, the writer considered that the active species for the polymerization is of a very short lifetime which is formed transiently in the reaction between trialkylboron and oxygen or oxygen compounds. Since most of the polymerizations stated above were conducted at room temperature in the presence of excess trialkylboron compared with oxygen, the active peroxide initially formed might have been rapidly converted into the inactive substances if the monomer had not been preliminarily added to the reaction system.

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C H A P T E R 2

ORGANOCALCIUM COMPOUND

Section 1. Introduction

Since the discovery of the Ziegler--Natta catalyst, there have been presented a number of papers which are concerned with the catalytic activity of organometallic compound for olefin polymerization. The central metallic elements of the organometallic compounds so far studied covers almost all the common metallic elements in the periodic table. The organometallic compounds of group I elements, such as lithium, sodium and potassium, have long been known to exhibit highly reactive behaviour toward the polymerization. Of the organic derivatives of group III elements, the aluminium compounds are the most widely known as component of "Ziegler--Natta" catalyst. As we reported before[1], organoboron compounds were found to be effective catalyst for vinyl polymerization in the presence of appropriate cocatalysts. Among the organometallic compounds of group II elements, zinc[2] or cadmium[3] alkyl was found to have interesting properties as polymerization catalyst. However, alkyl compounds of alkaline earth metals, i. e., calcium, strontium or barium, have not been isolated as yet, and the nature of organoalkaline earth metal compounds as polymerization catalyst seems to remain obscure.

The writer prepared an organocalcium compound, calcium zinctetraethyl, by the reaction of calcium metal with diethylzinc and studied the reactivity of this compound on various vinyl monomers. Acrylonitrile, methyl methacrylate and styrene have been found to be readily polymerized by this calcium compound[4]. Quinones and oxygen suppress the polymerization. A copolymerization study between styrene and methyl methacrylate using the calcium compound gave typical anionic monomer reactivity ratios. Results of kinetic study also supported anionic mechanism of the polymerization. Examinations on some physical properties of the polystyrene obtained showed the polymer to be crystallizable.

Section 2. Experimental

2-1. Reagents

Solvents

n-Hexane[5]: Commercial material was washed by sulfuric acid, then by water, dried with calcium chloride, distilled and dried with metallic sodium before use. B.p. 67 -- 86°C.

Benzene of extra-pure grade was washed by sulfuric acid, then by water, dried with calcium chloride, distilled and stored on metallic sodium before use. B.p. 80°C.

Diethyl ether of extra-pure grade was dried with metallic sodium and was used without further purification.

Monomers

Styrene[6] was washed by 10 % caustic soda, then by water, steam-distilled, dried with calcium chloride and distilled under reduced pressure. This was repeated just before use. B.p. 55°C./33 mm Hg.

Methyl methacrylate was washed by 10 % caustic soda, then by water, dried with calcium chloride, and distilled under reduced pressure before use. B.p. 50°C./124 mm Hg.

Acrylonitrile[7] was washed by 5 % sulfuric acid, then by 5 % caustic soda, dried with calcium chloride, distilled before use. B.p.77°C.

2-2. Organocalcium Compound

An organocalcium compound, calcium zinctetraethyl complex, $CaZn(C_2H_5)_4$, was prepared by the method of Gilman[8], starting from diethylzinc and calcium metal,

$$Ca + 2\ Zn(C_2H_5)_2 = CaZn(C_2H_5)_4 + Zn\ .$$

An example of recipe used for the investigations is shown below: a mixture of 60 ml. (0.6 mole) of diethylzinc, 12 g. (0.3 mole) of rasped calcium metal, and 20 ml. of dry benzene was heated slowly (over a period of 1 hr.) up to 110°C., and was stirred at this temperature for 7 hrs. This and all subsequent reactions were carried out under nitrogen. Toward the end of the reaction, the mixture turned to a thick suspension coloured in brownish black. This suspension was used as catalyst, diluted by benzene if necessary.

Diethylzinc used here was prepared from alkyl halide and zinc-copper couple[9]. Maximum yield 55 %, b.p. 112--115°C. (Ref. B.p.115 --

120°C.).

2-3. Polymerization Process

Polymerization was carried out in a sealed tube or in a test tube with a ground glass stopper; reaction mixture was allowed to stand or left rotating at a constant temperature. In some cases benzene (or others) was added to the reaction mixture as diluent. After a certain reaction time, methanolic hydrochloric acid was added to decompose the catalyst and stop further polymerization.

A typical example of polymerization process is as follows: To 0.05 mole (5.4 ml.) of methyl methacrylate was added 2 ml. (5 mole % for the monomer) of the suspension of the organocalcium compound. The reaction mixture immediately solidified on account of the polymer formation. Reaction temperature was kept at 10°C. After 20 hrs. methanolic dilute hydrochloric acid was added to the reaction mixture to precipitate the polymer. This was dissolved in chloroform and was washed by dilute hydrochloric acid to remove the decomposed catalyst. Polymer was reprecipitated by methanol, boiled with water to remove solvent and unreacted monomer, then dried in vacuo at 45°C. Extent of polymerization was 54.3 % and viscosity average degree of polymerization 5260.

2-4. Separation and Purification of Polymer

Polymer formed was separated from liquid phase by the addition of methanol to the reaction mixture. Separated polymer was boiled with

water for several hours to remove solvent and inorganic substances, and was dried at 40 -- 50°C. in vacuo to constant weight.

2-5. Molecular Weight Determination

Polymer was dissolved in a suitable solvent, and the intrinsic viscosity of the solution was measured by Ostwald's viscometer. Degree of polymerization was calculated by the equations given in Table I.

Table I. Viscosity -- D. P. Equation

Polymer	Solvent	Temp. (°C.)	Equation	Ref.
Polyacrylonitrile	Dimethyl formamide	25	$[\eta] = 1.66 \times 10^{-4} M^{0.81}$	10)
Polymethyl methacrylate	Chloroform	20	$[\eta] = 0.48 \times 10^{-4} M^{0.80}$	11)
Polystyrene	Toluene	30	$[\eta] = 1.2 \times 10^{-4} M^{0.79}$	12)

Section 3. Calcium Zinctetraethyl Complex

Organocalcium compound in the form of dialkyl calcium, CaR_2, has not yet been successfully isolated*). Gilman[8] prepared the organometallic compounds of calcium, strontium and barium by the reaction

*) Dimethyl compounds of calcium, strontium and barium were recently reported to be obtained by the reaction of these metals with methyl iodide in pyridine[13].

between diethylzinc and these alkaline earth metals, respectively. In the case of strontium Gilman isolated a complex $Sr(C_2H_5)_2 \cdot Zn(C_2H_5)_2$ which was formed by the reaction,

$$Sr + 2\ Zn(C_2H_5)_2 = Sr(C_2H_5)_2 \cdot Zn(C_2H_5)_2 + Zn\ .$$

According to Gilman, in the case of calcium too, the ether extract of the reaction mixture was found to contain a complex, the composition of which was confirmed analytically as $Ca(C_2H_5)_2 \cdot Zn(C_2H_5)_2$.

The reaction is,

$$Ca + 2\ Zn(C_2H_5)_2 = Ca(C_2H_5)_2 \cdot Zn(C_2H_5)_2 + Zn\ .$$

The writer prepared calcium zinctetraethyl complex, $CaZn(C_2H_5)_4$, by the method of Gilman, as shown in the experimental part.

The complex was found to have only a small solubility in ether or benzene; the extract by these solvents contained only a small amount of organometallic compound. Moreover, the extract showed little activity for vinyl polymerization. The finely dispersed particles of the reaction product were primarily composed of the complex and metallic zinc, together with a small amount of the unreacted calcium metal; unreacted diethylzinc, if any, would be present in the solution. However, metallic calcium or zinc was established to have no catalytic activity for vinyl polymerization. The catalytic activity of diethylzinc also was proved to be much smaller than the complex suspension. The suspension itself was used as catalyst.

Effective concentration of catalyst in the suspension system

Effective concentration of the calcium complex in the suspension system was determined by gas analysis in the following way. A certain

volume of the suspension system was mixed with an excess of dilute hydrochloric acid, and ethane and hydrogen evolved were analyzed,

$$CaZn(C_2H_5)_4 + 4\ HCl = 4\ C_2H_6 + CaCl_2 + ZnCl_2$$

$$Zn\ (or\ Ca) + 2\ HCl = H_2 + ZnCl_2\ (or\ CaCl_2)\ .$$

The quantity of ethane evolved from unreacted diethylzinc in the solution was calibrated. (This calibration was found to be less than one-tenth of the total gas evolution.)

With respect to a unit volume of the suspension, there was found a linear relationship between ethane evolution and the catalytic activity for vinyl polymerization, as seen in Figure 1.

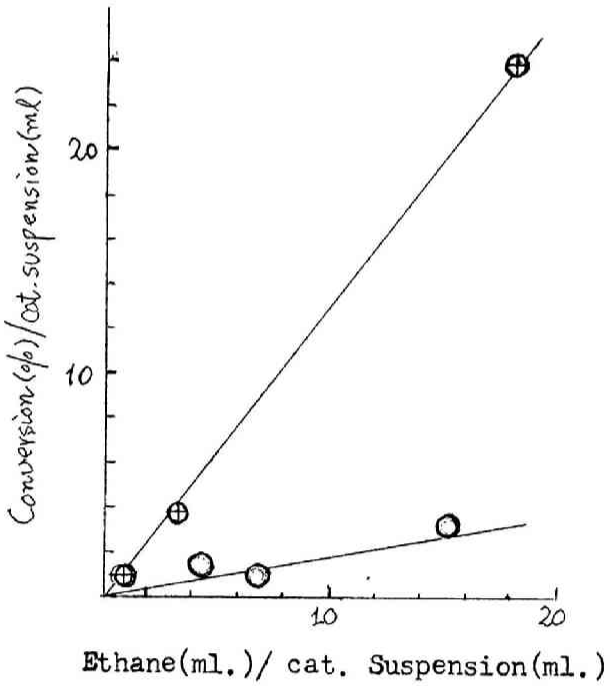

Fig. 1. Conversion-ethane quantity relation.

⊕, Methyl methacrylate (0°C., 90 mins.).

○, Styrene (60°C., 4 hrs.).

Section 4. Vinyl Polymerization by Calcium Zinctetraethyl

Experimental results of vinyl polymerization catalyzed by the calcium compound are shown in Table II.

Table II. Vinyl Polymerization by Calciumzinctetraethyl Complex[a)]

Monomer	Conversion(%)	D.P.
Acrylonitrile	48.2	410
Methyl methacrylate . .	54.3	5300
Styrene	9.6	5490

a) Monomer, 0.05 mole; catalyst, 5 % for monomer; 20 hrs. reaction at 10°C.; under nitrogen.

Vinyl acetate, and vinyl chloride were not polymerized by the calcium complex. Acrolein reacted violently to form a hard, insoluble polymer. In the case of vinyl acetate, there happened a sudden colouring of the reaction mixture immediately after the addition of the catalyst. Polymerization, however, did not occur. It may be considered that the organocalcium compound reacts with the functional group of vinyl acetate to cause another condensation reaction or decomposition of the monomer.

Section 5. Copolymerization

The results of copolymerization between styrene and methyl methacrylate are given in Table III and Figure 2.

Monomer reactivity ratios calculated from the table are $r_1 = 0.31$ and $r_2 = 17.1$ with styrene as monomer 1. Considering the reactivity ratios, the polymerization induced by calcium zinctetraethyl complex seems to be a typical anionic polymerization.

Table III. Copolymerization between Styrene and Methyl Methacrylate by Calciumzinctetraethyl Complex[a)]

Initial monomer ratio		Conversion (%)	Mole % of each component in the copolymer	
Styrene	Methyl methacrylate		Styrene	Methyl methacrylate
1	9	7.4	1.41	98.59
2	8	9.1	1.65	98.35
3	7	10.0	2.73	97.27
4	6	9.9	3.87	96.13
5	5	10.8	6.48	93.52
6	4	11.8	7.38	92.62
7	3	3.8	7.74	92.26
8	2	2.5	10.44	89.56
9	1	1.5	12.15	87.85

a) Total monomer, 0.1 mole; catalyst, 1.5 % for the monomer mixture; reaction time, 1 hr.; temp. 30°C.; under nitrogen.

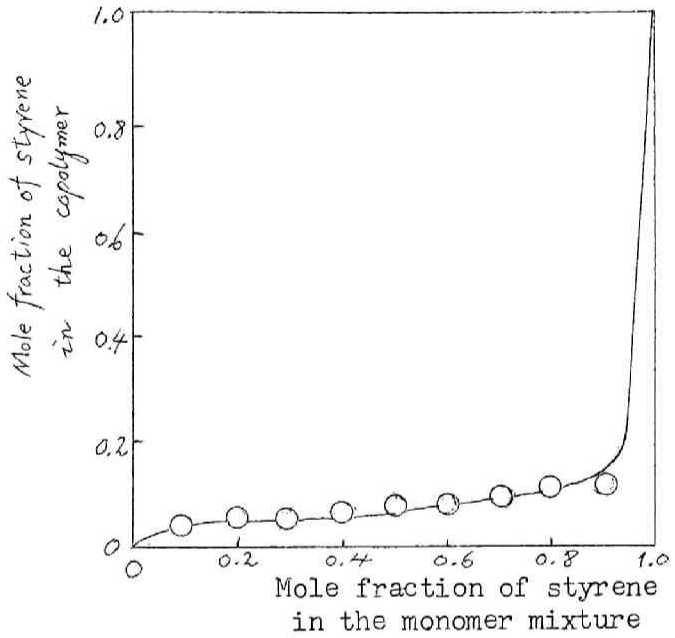

Fig. 2. Copolymerization between styrene and methyl methacrylate.

Section 6. Inhibitory Action of some Compounds

The rate of polymerization by calcium zinctetraethyl complex was decelerated by the addition of hydroquinone, benzoquinone or nitrobenzene, as shown in Table IV.

In the cases of quinones, there was observed change in colour of the system. The behaviour was quite reverse to the diethylcadmium catalyst[3], where quinones were effective cocatalysts for vinyl polymerization.

As seen in Table V, no marked effect of oxygen on the polymerization was observed for the relevant catalyst.

Table IV. Inhibitory Action of some Compounds on the Polymerization of Methyl Methacrylate[a)]

Inhibitor	Ratio of the inhibitor to the catalyst, (%)	Conversion (%)	D.P.
None	0	100	5260
Hydroquinone	50	71.0	3480
Benzoquinone	50	4.1	1840
Nitrobenzene	50	Little	----

a) Monomer, 0.1 mole; cat., used, 2.5 % for the monomer; 3 hrs.; 30°C.; under nitrogen.

Table V. Effect of Oxygen on the Polymerization

Exp. No.	Monomer	Gas phase	Conversion (%)	D.P.
2·3[a)]	Styrene	N_2	45.4	84
2·4[a)]	Styrene	Air	11.7	70
12·3[b)]	Methyl methacrylate	N_2	2.36	1650
12·4[b)]	Methyl methacrylate	Air	4.27	1500

a) Styrene, 0.0434 mole; cat., 3.37×10^{-5} mole; 75.5 hrs.; 40°C.

b) Methyl methacrylate, 0.0468 mole; cat., 1.38×10^{-6} mole; 90 min.; 0°C.

In case of styrene even inhibitory action of oxygen was observed.

Section 7. Comparison of the Reactivity of the Calcium Complex with other Organometallic Compounds

Reactivity of the organocalcium compound toward the vinyl monomers mentioned above is almost similar to that of the organoalkali compounds, which have so strong reactivity to polar monomers that cause explosive polymerization accompanied by side reactions, forming polymers of low molecular weight[14]. On the other hand, the alkali compounds exhibit moderate activities toward non-polar monomers such as styrene[15] or dienes[16]. Organobarium compound, e. g., barium zinctetraethyl, was found to show a catalytic activity for polymerization similar to the calcium compound[17]. Such a reactivity is characteristic for metal alkyls of elements which have small "electronegativity" values (alkali metals 0.8 -- 1.0; alkaline earth metals 0.9 -- 1.0).

As we reported before, organometallic compounds of metallic elements with larger electronegativities, e. g., zinc[2] (1.5), boron[1] (1.8) and others, can induce the vinyl acetate polymerization in the presence of oxygen compounds[1b]. In these cases, the polymerization is considered to be initiated by an unstable intermediate (for example, organic peroxide) arising from the reaction between organometallics and oxygen compounds. The polymerization reactions were proved to proceed according to a radical mechanism[1c].

On the other hand, polymerization by organoalkali compounds is initiated by alkyl anion from these compounds[18]. In case of organocalcium compound a similar mechanism may be considered (see results of

copolymerization and kinetic study).

Section 8. Kinetics

It was rather difficult to obtain reproducible quantitative results on account of heterogeneity of the catalyst system. Size and aging of the catalyst particles seemed to influence on the extent and the degree of polymerization as well as stereospecificity of the polymer formed.

Fairly well reproducible data of the methyl methacrylate polymerization in benzene were obtained from experiments carried out in sealed tubes under nitrogen by using the catalytic complex which is dispersed in benzene as finely as possible.

8-1. Temperature Dependence

Polymerization of methyl methacrylate in benzene solution was carried out at various temperatures to know the temperature dependence of the rate and the degree of polymerization.

The overall activation energy, E_{Rp}, found from Fig. 3 is 5.7 Kcal./mole for the methacrylate polymerization in benzene. This value is rather small and of the same order of magnitude as those found for the ionic polymerizations in literature[19].

The degree of polymerization showed a tendency to increase as the conversion became higher. The higher reaction temperatures also seemed to increase the degree of polymerization.

Table VI. Polymerization of Methyl Methacrylate at 20°C.[a)]

Exp. No.	Reaction time (min.)	Conversion (%)	$\bar{P}$
19·1	10	0.151	410
19·2	30	0.136	
19·3	60	0.351	460
19·4	95	0.300	
19·5	120	0.214	
19·6	150	0.476	530
19·7	210	0.529	
19·8	270	0.533	

a) Monomer, 4 ml.; benzene, 4 ml.; cat., 4.7×10^{-5} mole; under nitrogen.

Table VII. Polymerization of Methyl Methacrylate at 30°C.[a)]

Exp. No.	Reaction time (min.)	Conversion (%)	D.P.
20·1	10	0.111	
20·2	30	0.140	
20·3	60	0.146	
20·4	90	0.297	390
20·5	120	0.501	
20·6	150	0.820	620

a) Monomer, 4 ml.; benzene, 4 ml.; cat., 4.7×10^{-5} mole; under nitrogen.

Table VIII. Polymerization of Methyl Methacrylate at 45°C.[a)]

Exp. No.	Reaction time (min.)	Conversion (%)	D.P.
21·1	10	0.097	
21·2	30	0.443	530
21·3	60	0.388	
21·4	90	0.877	
21·5	120	1.150	710

a) Monomer, 4 ml.; benzene, 4 ml.; cat., 4.7×10^{-5} mole; under nitrogen.

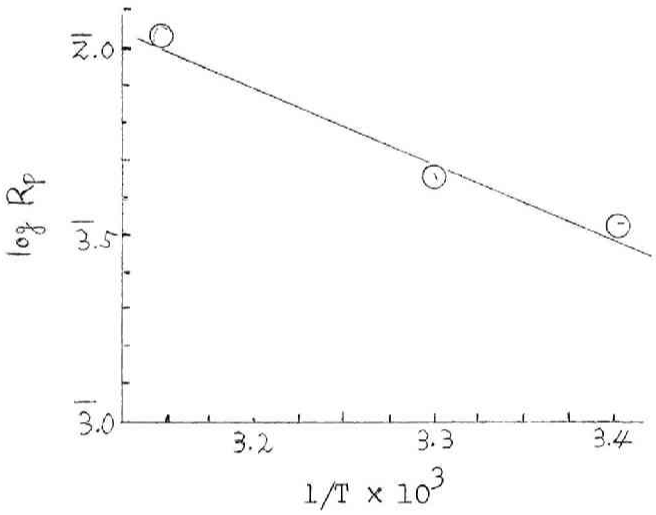

Fig. 3. Temperature dependence of the rate (methyl methacrylate in benzene)

8-2. Effect of the Initial Monomer Concentration

The dependency of the rate and the degree of polymerization upon monomer concentration is shown in Table IX and Figure 4.

Table IX. Effect of the initial Monomer Concentration[a)]

Exp. No.	Monomer conc. (mole/ℓ.)	Yield (g.)	D.P.
26·1	0.391	0.0217	1100
26·2	0.781	0.0543	1600
26·3	1.17	0.0598	1700
26·4	1.56	0.152	3300
26·5	1.95	0.135	3400
26·6	2.34	0.172	3100

a) Total volume (benzene solution), 12 ml.; cat., 4×10^{-4} mole; 1 hr.; 45°C.; under nitrogen.

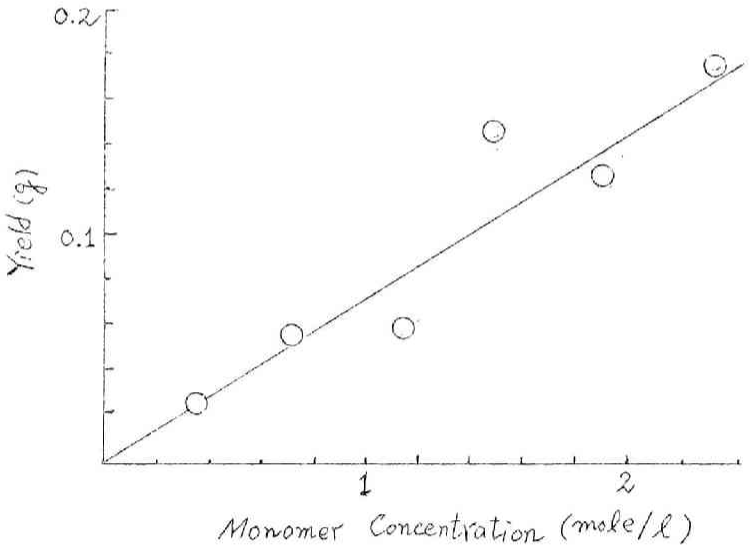

Fig. 4. Monomer concentration dependence of the rate.

As seen in Fig. 4, the overall rate shows a linear relationship to the initial monomer concentration. The degree of polymerization also increases linearly with the concentration of monomer.

8-3. Effect of the Catalyst Concentration

Effect of the catalyst concentration is shown in Table X and Figure 5.

Table X. Effect of the Catalyst Concentration[a)]

Exp. No.	Catalyst conc. (mole/ℓ.×10^{-3})	Conversion (%)	D.P.
6·1	1.25	2.94	2900
6·2	2.30	5.69	1300
6·3	4.50	16.2	2030
6·4	6.20	33.7	2780
6·5	8.79	32.2	2360
6·6	10.7	38.7	2080

a) Monomer, 0.0468 mole; in bulk; 90 min. at 0°C.; under nitrogen.

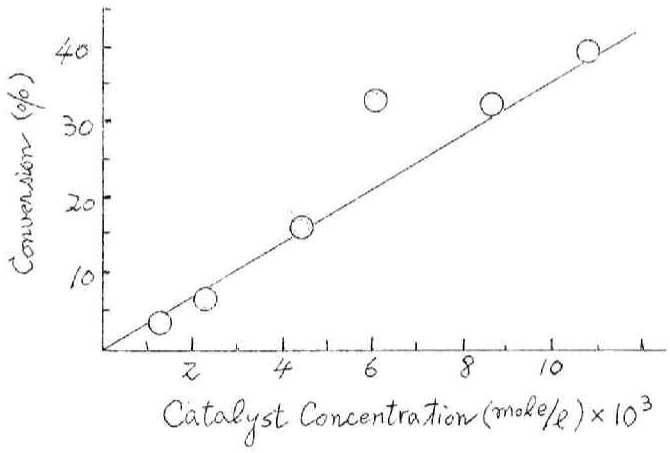

Fig. 5. Catalyst concentration dependence of the rate.

The rate is proportional to the catalyst concentration. The degree of polymerization, however, is almost independent of the concentration of the catalyst.

8-4. Kinetics

The above results indicate that the overall rate of polymerization, R_p, of methyl methacrylate is proportional to the initial monomer concentration, $[M]$, and to the catalyst concentration, $[C]$;

$$R_p \sim [M][C] \tag{1}$$

The degree of polymerization, $\bar{P}$, is proportional to the initial monomer concentration, but independent of the catalyst concentration;

$$\bar{P} \sim [M] \tag{2}$$

To make account of the relations (1) and (2), the following mechanism may be considered:

Initiation

$$C \xrightarrow{k_i} R^-$$

$$R^- + M \xrightarrow{k_1} RM^-$$

Propagation

$$RM_x^- + M \xrightarrow{k_p} RM_{x+1}^-$$

Termination

$$RM_x^- \xrightarrow{k_t} P$$

where C, R^-, M_x^- and P are the catalyst, catalyst anion, an x-mer anion and the dead polymer, respectively.

Assuming $k_1 \ll k_i$, at stationary state,

$$k_i[C] = k_t[RM_x^-]$$

Overall rate, R_p, therefore, will be

$$R_p = k_p[RM_x^-][M] = \frac{k_p\, k_i}{k_t}[C][M] \tag{3}$$

Degree of polymerization, $\bar{P}$, also will be

$$\overline{P} = \frac{k_p [RM_x^-][M]}{k_t [RM_x^-]} = \frac{k_p}{k_t} [M] \qquad (4)$$

Thus relations (1) and (2) may be explained. These kinetic results may make it possible to consider the mechanism of the polymerization to be anionic. However, the nature of the catalyst anion R^- remains obscured.

Section 9. Some Properties of Polymer by the Catalyst

9-1. Polystyrene

A sample of polystyrene prepared by calcium zinctetraethyl complex as catalyst was found to involve 13 % fraction insoluble in hot methyl ethyl ketone; infrared spectrum of the insoluble part distinctly showed the crystalline band[20] (Fig. 6).

An X-ray diffraction pattern of this polymer has shown discrete rings as seen in Fig. 7.

From the above results together with the large value of density ($d_4^{25} = 1.064$), the polystyrene by this catalyst is considered an isotactic polymer. In addition, the stereospecifity of polystyrene by the catalyst was found to depend on the activity and the size of the particle of the catalyst suspension.

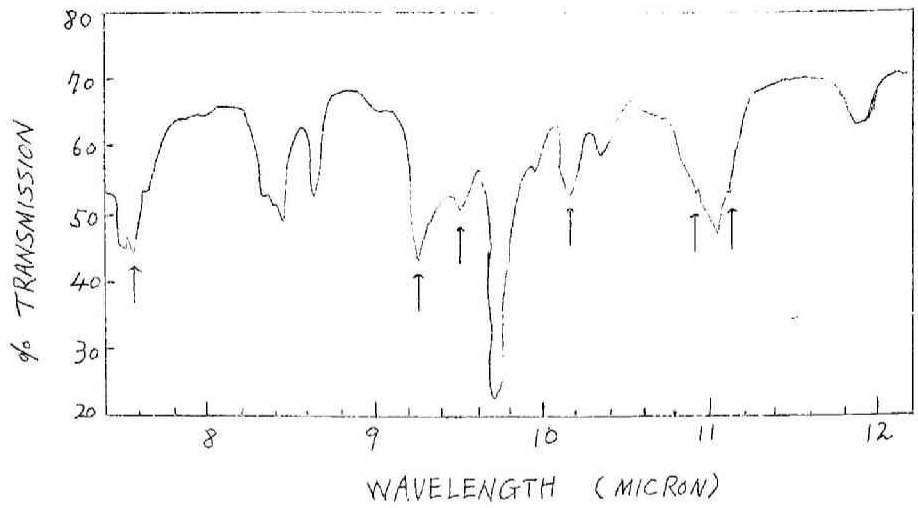

Fig. . Infrared spectrum of polystyrene.
Arrows indicate crystalline sensitive bands

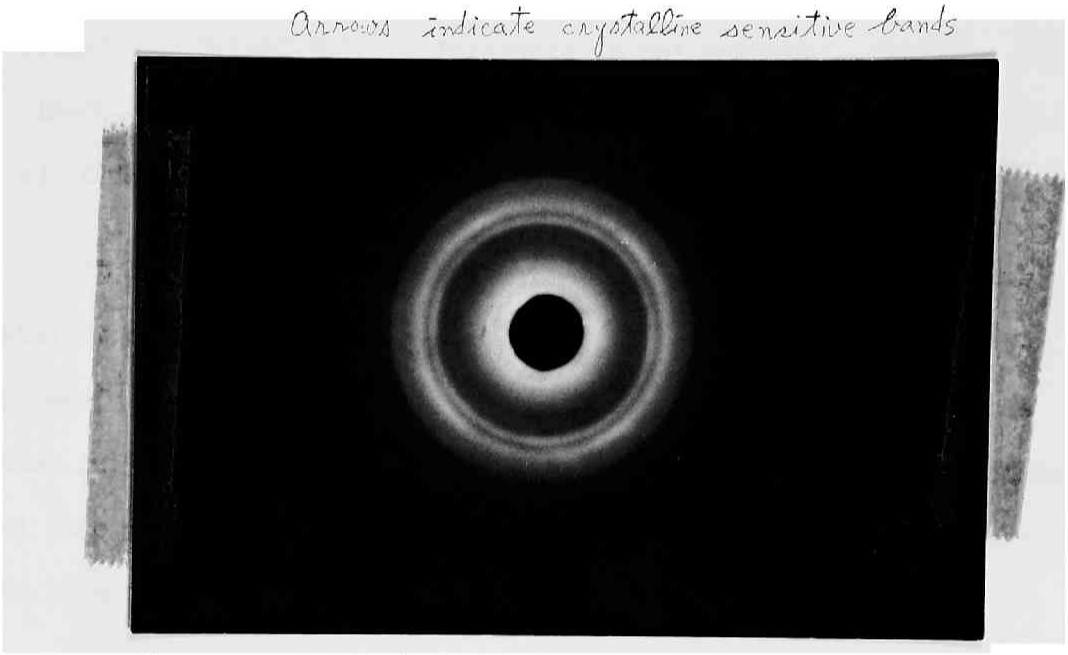

Fig. . X-ray diffraction photograph of polystyrene
Sample : Polystyrene film of 250 % stretch,
d_4^{25}, 1.064.

9-2. Polymethyl Methacrylate

Polymethyl methacrylate obtained by calcium zinctetraethyl complex as catalyst at room temperature was found to be insoluble in acetone, being quite different from the usual polymer. Chloroform solution of the fraction insoluble in hot acetone had Huggins' k' value which is distinguishable from that of the ordinary polymer (Table XI).

Table XI. Viscosity of Various Polymethyl Methycrylates

Sample No.	Catalyst	Solubility	(η) a)	k' a)
IY04-i	$CaZn(C_2H_5)_4$	Insoluble in hot acetone	3.25	0.548
IM-0	AIBN	Soluble in hot acetone	1.90	0.392

a) Chloroform solution; 20°C.

It has been found that the poly(methyl methacrylate) by this catalyst complex was a crystallizable polymer, and it was named F-polymer*). A typical example of the fractionation of F-polymer is shown in Table XII. The polymer samples were treated with 3-heptanone and were subjected to the infra-red and X-ray analysis. These results are illustrated in Figures 8 and 9.

Sample for these measurements was prepared in a form of film, usually from chloroform solution. The crystallization of the sample film was effected by swelling treatment with 3-heptanone at room temperature followed by gradual evaporation of the swelling agent. After the treatment the sample shows discrete X-ray diffraction pattern.

*) F-polymer is considered to correspond to 'Type III' polymer by Fox[21].

Without this treatment the sample was found to be amorphous by an X-ray diffraction study.

Table XII. Fractionation of F-polymer

Original sample	Solubility	Content of the fraction based on the original sample (%)	Sample No.
ICM-1	Soluble in cold acetone	15	ICM-3
	Insoluble in cold acetone	85	ICM-2'
ICM-2'	Soluble in cold chloroform	64	ICM-2
	Insoluble in cold chloroform	36	ICM-4[a)]

a) Soluble in boiling methyl ethyl ketone.

In Figure 10 is given the infra-red spectrum of ordinary (radical) poly(methyl methacrylate), in comparison with Figure 9.

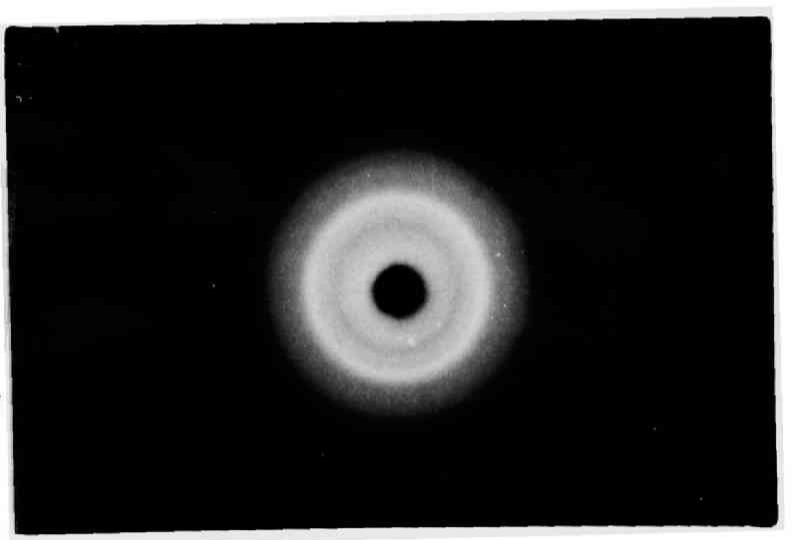

Fig. 8. X-ray diffraction pattern of crystalline F-polymer.

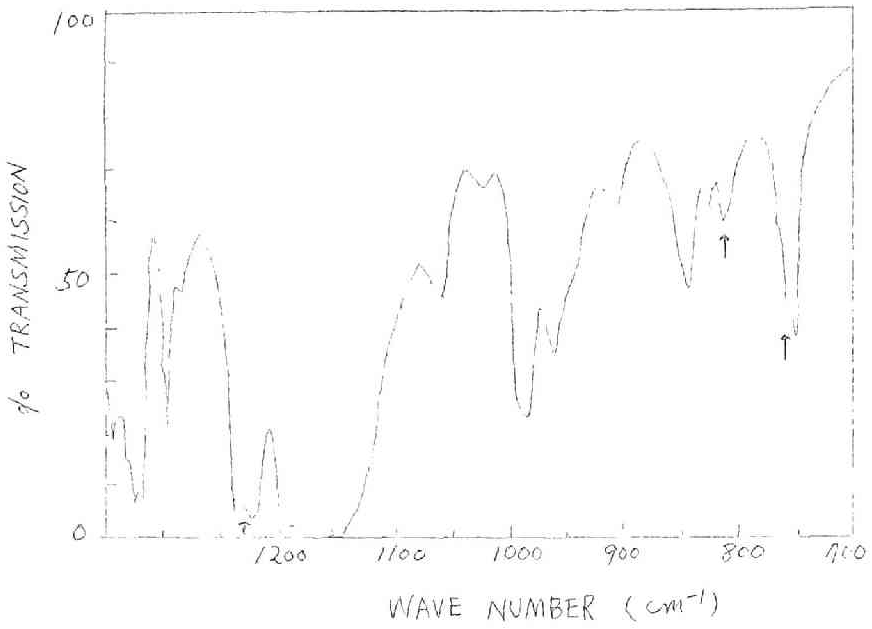

Fig. 9. Infrared absorption spectrum of F-polymer (ICM-4) in the crystalline state.
Arrows indicate the characteristic bands.

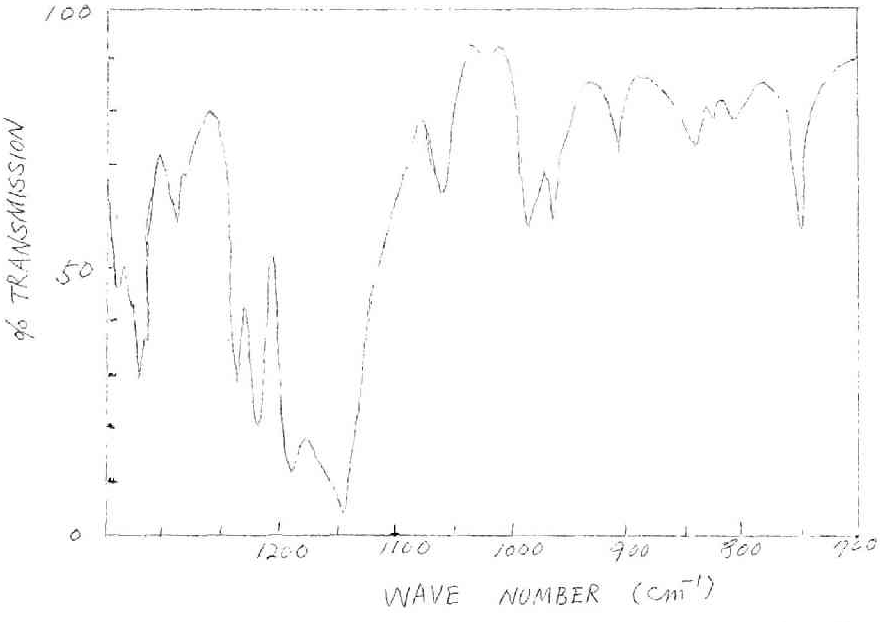

Fig. 10. Infrared absorption spectrum of usual radical poly(methyl methacrylate).

There are seen some characteristic bands in the spectrum of F-polymer. These characteristic bands are observed even before the crystallization treatment, however some of these bands were observed to be enhanced in intensity by the crystallization. Detailed assignment of these characteristic bands will not be described in this paper.

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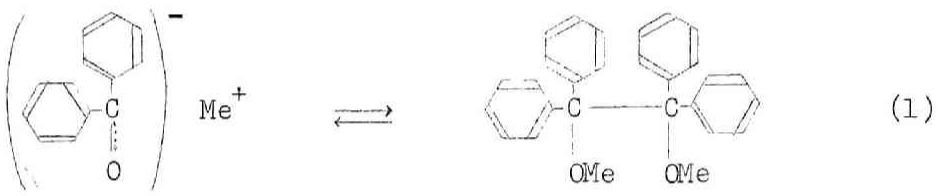
C H A P T E R 3

METAL KETYL

Section 1. Introduction

Non-enolizable ketones, e. g. aromatic ketones such as benzophenone, have long been known to give deeply coloured addition products by the reaction with alkali metals[1]. Studies by E. Müller[2] on the magnetic property of the reaction product of benzophenone and alkali-metal proved it to be an equilibrium mixture of radical-ion pair (I) and pinacolate (II).



(1)

(I), deep blue (II)

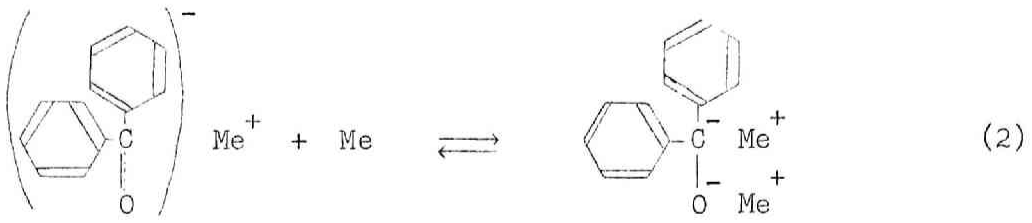
Me = Li, Na, K.

In the solution of dioxane, however, ketyl is said to exist completely as the ion pair (I)[3].

The metal ketyl (I) can form a di-alkali complex (III) with one more alkali metal atom where the metal is present in excess.

Some papers including our short communication[4] on the catalytic

activity of the ketyl for vinyl polymerization were recently published[5,6].



(I), deep blue (III), reddish violet (2)

Smith[5] reported vinyl polymerization by the benzophenone-sodium complex. He found that an excess of the sodium metal was necessary for the polymerization of styrene, contrary to methyl methacrylate. Crystallizable polystyrene was obtained in the polymerization using toluene as the solvent. However, only amorphous polymethyl methacrylate was formed under the conditions studied by him.

Zilkha et al.[6] studied vinyl polymerization by various ketyls. The reactivity of the vinyl monomers was found to be in the following order: Acrylonitrile $>$ methyl methacrylate $\gg$ styrene. The catalytic activity of the metal ketyl was proportional to the electropositivity of the attached metal. A copolymerization experiment with acrylonitrile and styrene as comonomers resulted in the formation of homo-polyacrylonitrile. Based on the study of the structure of this polymer, they proposed that the polymerization was initiated by the alkoxide part of the ketyl molecule.

In our previous paper[4] the writer reported that the character of the ketyl-initiated vinyl polymerization was appreciably affected by the variation in the kind of the ketone, metal and solvent. There were

also mentioned the effect of metal on the copolymer composition and the characteristic behaviour of the dimetal complex (III) towards the styrene polymerization compared with (I).

These reports, however, have not made sufficient considerations on the mechanism of ketyl-initiated polymerization. Difference in the reactivity between ketyl (I) and dimetal complex (III) also remains obscured.

Our further investigation made clear the difference between (I) and (III): Only the latter can induce the styrene polymerization, where the formation of a living polymer was observed. A study on the copolymerization by the ketyl or the dimetal complex showed the polymerization to be typically anionic. In the present chapter, consideration will also be made, on the possible mechanism of the polymerization.

Section 2. Experimental

2-1. Reagents

Monomers (styrene, methyl methacrylate, methyl acrylate and acrylonitrile) and solvents (n-hexane, benzene and ether) were purified by the usual methods[7].

Tetrahydrofuran and dioxane were purified by distillation in the presence of benzophenone sodium ketyl. Alkali metals were used without further purification. Ketones were purified by recrystallization if necessary.

Ketyl was prepared by the reaction of alkali metal with an excess of the ketone in tetrahydrofuran or dioxane[4]. The dimetal complex was prepared in a similar way with an excess of the metal. The solutions of the complexes obtained were filtered under nitrogen to remove unreacted metal. The effective concentration of the catalyst was determined by alkalimetry of the solution of the hydrolyzed complex.

2-3. Polymerization

Polymerization was carried out under an atmosphere of nitrogen in a test tube with ground-glass stopper or in a ground-glass connected apparatus excluded from air, especially in the case of low-temperature polymerization. Nitrogen used in the polymerization was purified by passing it successively through Fieser's solution, sulfuric acid and ketyl solution to remove the trace of water and oxygen. The polymerization was stopped by the addition of a few drops of water, methanol or hydrochloric acid to the reaction mixture. The polymer formed was separated and purified in the usual way[7]. The degree of polymerization was determined by measuring the intrinsic viscosity of the polymer in a suitable solvent[7].

Section 3. Catalytic Activity of Mono- and Di-metal Complex

The activity of the monometal complex (ketyl) (I) and the dimetal complex (III) of benzophenone, used as catalysts for the vinyl polymerization, was studied. Table I shows the results of the polymerization in which potassium was used as the alkali metal component.

Table I. Vinyl Polymerization by Benzophenone-potassium Complexes[a)]

Catalyst (mole %)	Monomer (ml.)	Solvent (ml.)	Time (hrs.)	Extent of polymerization(%)	D.P.
Benzophenone-potassium ketyl(3)	Acrylonitrile (10)	Dioxane(5)	20	31.5	----
Benzophenone-potassium ketyl(6)	Methyl methacrylate(2)	Ether (5)	20	59.2	120
do.	do.	Hexane (5)	20	99.8	220
do.	Styrene (10)	Ether (5)	20	0	----
do.	Styrene (10)	Hexane (5)	20	0	----
do.	Vinyl acetate (10)	Hexane (5)	20	0	----
do.	Methyl acrylate (10)	Ether (5)	20	45.0	----
Benzophenone-dipotassium (2)	Acrylonitrile (5)	Dioxane(1)	--	Explosive	----
do.	Methyl methacrylate (5)	Dioxane(1)	7	78.3	170
do.	Styrene (5)	Dioxane(1)	7	100	2500
do.	Vinyl acetate (5)	Dioxane(1)	7	0	----

a) Polymerization at room temperature.

The difference in the behaviour of the two complexes, (I) and (III), toward the styrene polymerization is seen clearly in Table I. When the solution of ketyl (I) was added to styrene, the blue colour of the ketyl

was fairly stable and no polymerization took place. On the contrary, when the dimetal complex (III) (reddish violet) was added to styrene monomer, there occurred a sudden change in colour of the reaction mixture to blue and a rapid polymerization of styrene resulted. Acrylonitrile and methyl methacrylate were rapidly polymerized by ketyl (I) and dimetal complex (III), during which the colour of these complexes instantly disappeared. Vinyl acetate and vinyl chloride were not polymerized by these complexes; some reactions with the functional groups of these monomers seemed to take place.

Complexes of other metals than potassium were found to have nearly the same catalytic activity. Apparently the activity of the complexes seemed proportional to the electropositivity of the used metal, as shown in Table II. In general, the dialkali complex had a greater activity than the ketyl. For example, the benzophenone lithium ketyl had much a lower activity for acrylonitrile than the sodium or the potassium ketyl, and gave only the trace of a polymer under the given conditions. Benzophenone dilithium, on the other hand, polymerized acrylonitrile in a good yield (Table II).

Section 4. Formation of living Polymer by the Dimetal Complex

In the case of the styrene polymerization by benzophenone dialkali complex, a rapid and quantitative polymerization as well as a change in

the colour of the reaction mixture*) may make it possible to expect the formation of a living polymer.

Table II. Polymerization of Acrylonitrile and Methyl Methacrylate by Benzophenone-Alkali Complexes[a)]

Catalyst (mole %)	Monomer (ml.)	Solvent (ml.)	Time (hrs.)	Extent of polymerization (%)
Li-ketyl (6)	Acrylonitrile (10)	Dioxane (7)	50	trace
Na-ketyl (7)	Acrylonitrile (2)	Dioxane (5)	70	21.4
K-ketyl (7)	Acrylonitrile (10)	Dioxane (5)	50	31.5
Li-ketyl (6)	Methyl methacrylate (10)	Dioxane (7)	50	18.2
Na-ketyl (1)	Methyl methacrylate (5)	Tetrahydrofuran(2)	50	63.2
K-ketyl (9)	Methyl methacrylate (2)	Dioxane (2)	50	90.7
di-Li complex(2)	Acrylonitrile (5)	Tetrahydrofuran(2)	7	4.4
di-Na complex(1)	Acrylonitrile (5)	Tetrahydrofuran(1)	--	Explosive
di-Na complex(1)	Methyl methacrylate (5)	Tetrahydrofuran(2)	7	99.6

a) Polymerization at room temperature.

The polymerization of styrene seemed to proceed instantly to give a quantitative yield. If there is formed a living polymer in the reaction system, the addition of a second monomer will result in the forma-

*) Red colour of the benzyl anion was observed in case of the bulk polymerization.

tion of a block polymer[8]. To a mixture of 5 ml. of styrene and 10 ml. of tetrahydrofuran cooled to -70°C. benzophenone dipotassium (6 mole % for the monomer) was added. After 1 hour**), 10 ml. of methyl methacrylate were added. After standing for one and a half hour, the polymer was separated by precipitation with methanol containing hydrochloric acid. The polymer obtained was fractionated by cyclohexane and acetonitrile[8,9], then the composition of each fraction was determined by the elemental analysis. The results are summarized in Table III.

Table III. Fractionation of the Block Copolymer[a]

Fraction No.	Solubility	Content in the original polymer (%)	Methyl methacrylate content of the fraction (mole %)
1	Soluble in cold acetonitrile	31.2	99.7
2	Soluble in cold cyclohexane	2.5	7.9
3	Soluble in hot cyclohexane	25.0	33.6
4	Insoluble part: Soluble in hot acetonitrile	30.1	89.9
5	Insoluble part: Soluble in benzene	trace	----

a) Original polymer, $\eta_{sp}/c = 0.29$ (in toluene, 30°C.; $c = 0.27$ g./100 ml.).

Inspection on the infrared absorption spectrum of fraction No. 3 (insoluble in cold cyclohexane and hot acetonitrile) confirms that the

**) Styrene was proved to be polymerized to a quantitative yield under the same condition.

fraction is a styrene -- methyl methacrylate block copolymer. When styrene was added as the second monomer instead of methyl methacrylate to the reaction mixture, in which styrene was previously polymerized quantitatively stated above, an increase in the molecular weight of the polystyrene was observed. From these points of view, it is very probable to assume the formation of a living polymer during the course of the polymerization of styrene by the dimetal complex.

Section 5. Copolymerization

Results of copolymerization of acrylonitrile with methyl methacrylate by benzophenone ketyl are shown in Table IV. As seen in Table IV, the copolymer composition showed the ketyl-initiated polymerization to be typically anionic. The degree of the incorporation of acrylonitrile into the copolymer seems to increase in the order of the electropositivity of the metal component in the relevant ketyl used as the catalyst. The composition of the copolymer, however, is independent of the polar nature of the solvent.

Results of copolymerization by the dimetal complex are summarized in Table V. Polymerization by dimetal complex is also considered to be typically anionic from the above results.

Table IV. Copolymerization of Acrylonitrile and Methyl Methacrylate by Benzophenone-Ketyls[a)]

Alkali metal of the ketyl	Solvent	Acrylonitrile in the initial monomer mixture (mole %)	Acrylonitrile in the copolymer (mole %)
Li	Benzene	92.9	92.4
Li	Benzene	83.7	88.7
Li	Benzene	69.1	89.9
Li	Benzene	45.7	87.5
Li	Dioxane	92.9	91.4
Li	Dioxane	83.7	87.2
Li	Dioxane	69.1	89.7
Li	Dioxane	45.7	85.1
Na	Benzene	92.9	95.4
Na	Benzene	83.7	91.5
Na	Benzene	69.1	90.2
K	Benzene	80.0	92.3
K	Benzene	60.0	90.2
K	Benzene	40.0	89.1
K	Benzene	20.0	80.3

a) Polymerization at room temperature; solvent: Twice the volume of the monomer; extent of polymerization: Smaller than 15 %.

Table V. Copolymerization by Benzophenone-Dialkali Complexes[a)]

Alkali metal	Monomer mixture	Extent of polymerization (%)	Methyl methacrylate in the copolymer (mole %)
Li	Styrene--methyl methacrylate	9.2	91.0
Li	Acrylonitrile--methyl methacrylate	2.5	10.6
Na	Styrene--methyl methacrylate	14.5	95.4
Na	Acrylonitrile--methyl methacrylate	0.7	9.1
K	Styrene--methyl methacrylate	20.0	95.6

a) Initial monomer ratio 1 : 1; total monomer: 0.05 mole; without solvent; catalyst: 2 mole %; room temperature.

Section 6. Effect of Ketone and Solvent

Table VI. Activity of Sodium-Ketyls for Methyl Methacrylate Polymerization[a)]

Ketone	Colour of the ketyl	Reaction
Benzophenone	Deep blue	Instantaneous disappearance of the colour with rapid polymerization
Michler's ketone	Deep blue	do.
Benzil	Violet	Colour remains stable without polymerization
Fluorenone	Brown	Slow disappearance of the colour with mild polymerization
Xanthone	Deep blue	Disappearance of the colour with slow polymerization

a) Reaction at room temperature.

Results of the qualitative experiment on the catalytic activity of various sodium ketyls for the methyl methacrylate polymerization are given in Table VI. All the ketyls studied could induce the polymerization of acrylonitrile. However, the catalytic activities of the ketyls vary appreciably with the structure of the ketone component as seen in Table VI.

Effects of solvents on the polymerization of methyl methacrylate were also noticeable, as given in Table VII.

In general, a larger extent of polymerization was observed in nonpolar solvents than in polar solvents.

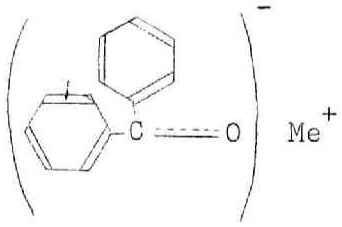
Table VII. Polymerization of Methyl Methacrylate by some Ketyls in Various Solvents[a)]

Monomer (ml.)	Solvent (ml.)	Catalyst (mole %)	Extent of polymerization (%)	D.P.
10	Dioxane(7)	Benzophenone-Li-ketyl (6)	18.2	320
10	Ether (7)	Benzophenone-Li-ketyl (6)	0	----
10	Benzene(7)	Benzophenone-Li-ketyl (6)	29.2	820
10	Hexane (7)	Benzophenone-Li-ketyl (6)	32.8	830
5	Dioxane(5)	Michler's ketone-Na-ketyl (0.8)	2.9	4100
5	Ether (5)	Michler's ketone-Na-ketyl (0.8)	4.0	4400
5	Benzene(5)	Michler's ketone-Na-ketyl (0.8)	11.3	3900
5	Hexane (5)	Michler's ketone-Na-ketyl (0.8)	35.0	2900

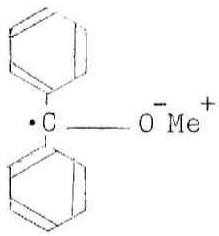
a) Reaction time: 50 hrs.; reaction temperature: 25°C.

Section 7. Discussion

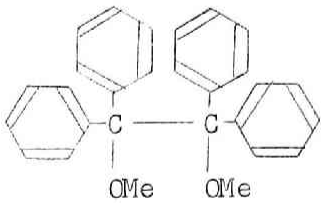
7-1. Initiation



(I)



(I')



(II)

The structure of metal ketyl (I) is frequently written as formula (I'). However, ketyl is quite different in reactivity from alcoholate RO^-Me^+; the latter does not polymerize methyl methacrylate[10].

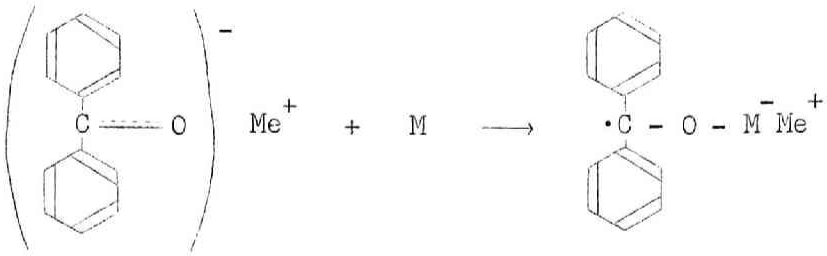
The unpaired electron of ketyl anion is not localized on the carbonyl carbon but spreads over the whole conjugated system. The negative charge of ketyl is also not completely localized on the oxygen atom, in contrast to the alkoholate ion. This structure may account for the median reactivity of ketyl anion which is between alcoholate and carbanion (Table VIII).

Table VIII. Activity of Catalysts for Anionic Polymerization[a)]

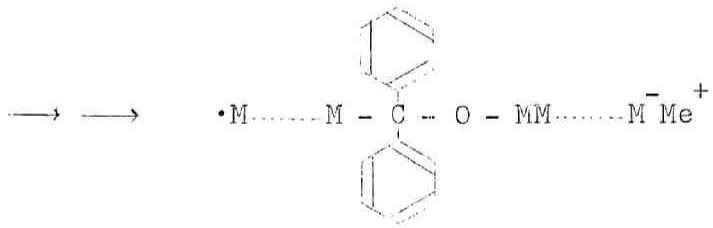
Monomer (e-value) / Catalyst	Acrylonitrile (1.2)	Methyl methacrylate (0.4)	Styrene (-0.8)
R^-Me^+	+	+	+
$(Ar_2C{=}O)^-Me^+$	+	+	-
RO^-Me^+	+	-	-

a) Me: alkali metal; +: polymerization; -: no polymerization.

As mentioned by Smith[5], propagation may proceed at both the ionic and radical ends of ketyl (I) in a way similar to the lithium-initiated polymerization[9]:



(IV)



(3)

(M: Monomer)

If this reaction mechanism were true, the relative rates of propagations at the both ends had been changed in response to the variation in the polarity of the solvent, which might result in the formation of copolymers having different monomer composition. Experimental results (Table IV), however, showed no effect of solvent on the copolymer composition. Thus, reaction of type (3) is improbable. The radical end of the growing polymer (IV) is considered too stable to attack the double bond of monomer. It is probably stabilized by recombination or hydrogen abstraction. According to Zilkha et al.[6], the initiation reaction is effected by the alkoxide end of the ketyl in the polymerization of acrylonitrile. This may be probably true in the case of the methyl methacrylate polymerization, even if it has not been actually verified

7-2. Propagation and Termination

We consider that the initiation and propagation reactions proceed by the 1,4-addition of organometallic compounds to the α,β-unsaturated carbonyl (or cyano) system.

Initiation

$$\text{Ketyl}^{-}\text{Me}^{+} + \text{C=C-C=O} \longrightarrow \underset{\text{(V)}}{\text{Ketyl-C-[C=C=O]}^{-}\text{Me}^{+}} \quad (4)$$

Propagation

$$\begin{aligned}&\text{Ketyl-C-C=C=O}^{-}\text{Me}^{+} \longrightarrow \text{Ketyl-C-C(-[C=C=O]}^{-}\text{Me}^{+}\text{)-C=O} \\ &+ \quad \text{C=C-C=O} \qquad\qquad\qquad\qquad\qquad\qquad (5)\\ &\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{(VI)}\end{aligned}$$

Conjugated system in the dotted line of (V) and (VI) is regarded as an enolate ion. Such an ionic structure seems to be possible only when the electronegativity of the metal is very small. Metals with larger electronegativity, presumably, make the conjugated system an undissociated enolate salt, C=C-OMe, which cannot effect further propagations. Propagation will proceed by the repetition of the addition of the enolate ion to the conjugated carbonyl system. Instead of reaction (5), reaction of type (6) may take place,

$$\begin{aligned}&\text{Ketyl-C-[C=C=O]}^{-}\text{Me}^{+} \longrightarrow \text{Ketyl-C-C=C-O} \\ &+ \quad \text{C=C-C=O} \qquad\qquad\qquad\qquad\qquad\qquad (6)\\ &\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{C-[C=C=O]}^{-}\text{Me}^{+}\end{aligned}$$

However, stereochemical and energetic considerations favour reaction (5)*).

The mechanism of the polymerization catalyzed by the ketyl may be extended to cases of general anionic polymerizations, where we assume again the formation of the enolate ion structure. In the previous papers[7,11], we suggested that a necessary condition for a metal alkyl to be a catalyst for an anionic vinyl polymerization is that the electronegativity (x) of the metal is smaller than 1.25. In this sense, alkyl derivatives of alkali and alkaline earth metals ($x = 0.8$ -- 1.0) qualify as catalysts for anionic polymerization because of the easiness in the formation of the enolate ion structure.

Since stereoregular polymethyl methacrylate was obtained under certain conditions using the ketyl catalyst, specific orientation of the monomer to the polymer end is quite probable in the 1,4-addition propagation reaction[12]. Enolate ion (VI) grows to a high polymer to precipitate out of the reaction system. 1,2-Addition to carbonyl group may also result in the termination[13].

Prominent effects of solvents on the polymerization of methyl methacrylate (Table VII) may be interpreted in terms of the change in the ratio of the rates of the competing reactions such as 1,4-addition reactions (4) and (5), stabilization of the propagating enolate ion and 1,2-addition to carbonyl group, in various solvents.

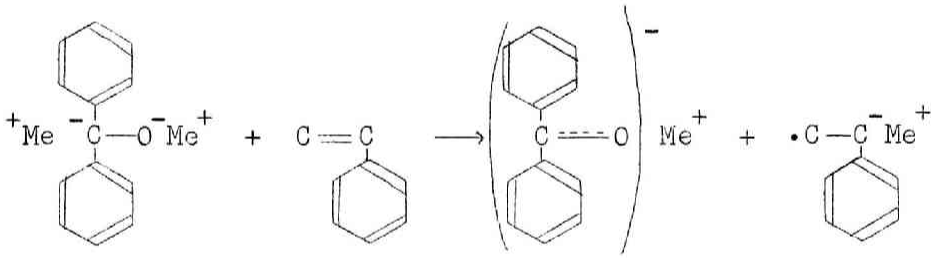
---

*) New bonds formed in (5) are two C-C and one C=O, in (6), two C-O and C=C. Summation of bond energies in each case is: 2C-C + C=O = 2 x 66 + 160 = 292; 2C-O + C=C = 2 x 77 + 113 = 267 (kcal./mole).

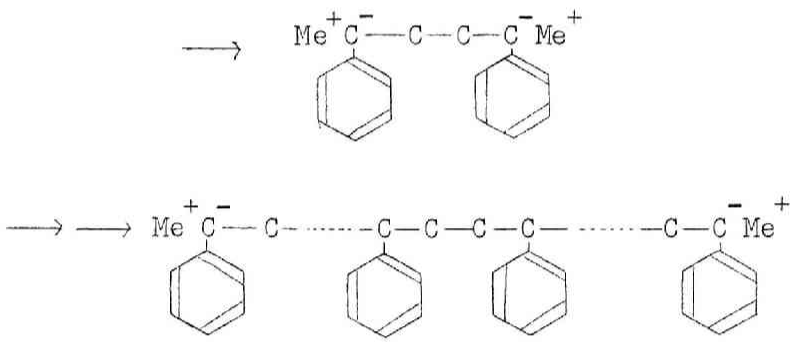
The change in the polarity of solvents will also influence the rate of the initiation by changing the stability of ketyl ion pair (I) or the degree of dissociation of pinacolate (II) to ketyl (I). The structure of ketone component of ketyl will effect upon the polymerization similarly (Table VI).

7-3. Reactivity of Dialkali Complex

In the polymerization of styrene by dimetal complex, electron transfer type reaction (7) may be considered.



(III), reddish violet (I), deep blue



(7)

red

(III) has one more electron than ketyl (I) and may readily cause the one electron transfer (7). Recently we found the formation of a

living polymer in the reaction between styrene and dialkali metal adducts of triarylboron[14]. In this case also, monoalkali metal adducts could not induce the polymerization of styrene.

Section 8. Properties of Polymer

The writer previously reported the preparation of crystallizable polymethyl methacrylate by some organometallic compounds[15]. By examination on the infrared absorption spectrum of polymethyl methacrylate obtained by ketyl or dimetal complex, the formation of F-type polymer[15] was confirmed (Table IX).

Table IX. Polymerization of Methyl Methacrylate

Sample No.	Catalyst	Solvent (ratio in volume to monomer)	Temp. (°C.)	Type[15]
MN-0-7	Michler's ketone-Na-ketyl	Benzene (1)	20	F
MN-0-8	Michler's ketone-Na-ketyl	Hexane (1)	20	F
M-104	Benzophenone-Li-ketyl	Tetrahydrofuran (1)	5	Conventional
M-106	Benzophenone-Li-ketyl	Benzene (2.5)	5	F
M-352	Benzophenone-di-Li	Toluene (1)	5	F
M-351	Benzophenone-di-Li	Ether (1)	5	F
M-302	Benzophenone-di-Li	Dioxane (1.7)	5	Conventional
MTB	Benzophenone-di-K	Tetrahydrofuran(0.6)	5	Conventional

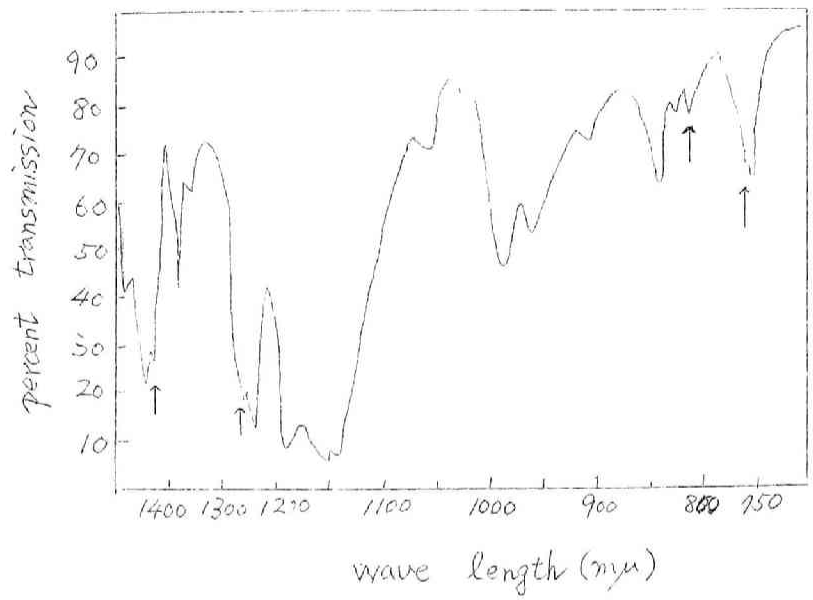


Fig. 1. Infrared absorption spectrum of type-F polymethyl methacrylate (Sample, M-352). Arrows indicate the characteristic bands.

Fig. 1 shows the infrared absorption spectrum of the sample M-352. Smith[5] reported that there is formed only an amorphous polymethyl methacrylate by the use of benzophenone complex and it is very interesting that the nature of the ketone and metal have also marked influence upon the stereospecificity of the polymers to be formed.

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C H A P T E R 4

ORGANOMERCURY COMPOUND

Di-n-BUTYLMERCURY -- METAL HALIDE SYSTEM

Section 1. Introduction

A large variety of organometallic compounds has recently been studied on the behavior as polymerization catalyst for olefins and polar vinyl monomers[1]. However, there have been few investigations on organomercury compounds, except for the report by M. M. Koton[2], who described some dialkylmercuries as initiator for vinyl polymerization. No detailed consideration on the catalytic activity have been made as yet. According to the report by Koton, the more unstable the dialkylmercury is, the more active as polymerization catalyst; dicyclohexylmercury and dibenzylmercury are highly active, on the contrary, diphenylmercury has lower activity, dihexylmercury, dinaphthylmercury and phenylmercuric bromide being inactive.

It is well-known that the carbon-mercury bond is weak[3] enough to be decomposed radically by the action of ultraviolet light or X-ray. Therefore, vinyl polymerization by dialkylmercury mentioned above may be considered to proceed by a radical mechanism.

The writer examined the catalytic activity of di-n-butylmercury --

metal halide system for vinyl polymerization. Di-n-butylmercury itself is incapable of initiating vinyl polymerization under usual conditions. Binary systems composed of di-n-butylmercury and some metal halides were found to be excellent initiators for vinyl polymerization. The kind of effective metal halide depends upon the kind of vinyl monomers to be polymerized. $ZnCl_2$, $SbCl_3$ and $BiCl_3$ are especially active cocatalysts.

Ziegler catalyst, which is also an organometallics -- metal halide system, has been considered to polymerize olefins by an anionic mechanism. However, the action of Ziegler type catalyst in the polymerization of polar vinyl compounds has not been made clear as yet.

Concerning with this, and considering the particular behavior of mercury salts in various organic reactions, it is interesting to examine the properties of di-n-butylmercury -- metal halide system.

Section 2. Experimental

2-1. Reagent

n-Hexane was washed with sulfuric acid, dried over calcium chloride, and was distilled. The distillate was dried over metallic sodium. B.p. 67 -- 68°C.

n-Heptane was purified by the same method as hexane. B.p. 97 -- 98°C.

Benzene was washed with sulfuric acid, then with water, dried over

calcium chloride, and was distilled. The distillate was dried over metallic sodium. B.p. 80°C.

Diethyl ether was dried over metallic sodium and was distilled.

Dioxane was refluxed over metallic sodium for several hours, then was distilled. B.p. 100 -- 101°C.

Ethyl acetate was dried over anhydrous potassium carbonate, then was distilled. B.p. 75 -- 76°C.

Styrene was washed successively with 10 % solution of sodium hydroxide and with water, then was steam-distilled. Distilled styrene was dried by calcium chloride and was distilled again under reduced pressure (B.p., 55°C./33 mm Hg.). A distillation was repeated in vacuo immediately before use.

Vinyl acetate was washed with a saturated solution of sodium bisulfite, then with water, dried over anhydrous potassium carbonate, and was distilled. B.p. 72 -- 73°C.

Methyl methacrylate was successively washed with 5 % caustic soda solution, then with water, dried over calcium chloride, and was distilled in vacuo. B.p. 50°C./124 mm Hg.

Methyl acrylate was purified by the same method as methyl methacrylate, B.p. 80°C.

Acrylonitrile was washed with 5 % sulfuric acid, then with 5 % caustic soda solution, dried over calcium chloride, and was distilled. B.p. 77°C.

Di-n-butylmercury, $(n\text{-}C_4H_9)_2Hg$, was prepared by the reaction of n-butylmagnesium bromide with mercuric chloride[4]. Yield, 65 %, B.p. 95

-- 97°C./10 mm Hg. (Ref. 4, 117°C./18 mm Hg.).

Metal halide :

In most cases the commercial materials of the highest grade were used without further purification. They are used as solution in a suitable solvent if necessary.

2-2. Polymerization Reaction

Polymerization reaction was carried out in a sealed tube at constant temperature leaving to stand or rotating. After a definite time interval, the reaction mixture was added by a non-solvent containing hydrochloric acid to separate polymer formed. The polymer was carefully washed to remove organomercury compound and treated by boiling water to remove solvent and inorganic substances, then dried at 45 -- 50°C. in vacuo to constant weight. Toxicity of dialkylmercury remaining in the washing may be avoided by adding concentrated hydrochloric acid. Dialkylmercury is converted to alkylmercury chloride by the treatment[5] and the volatility is much lowered.

2-3. Molecular Weight Determination

Polymer was dissolved in a suitable solvent and the solution viscosity was measured by Ostwald's viscometer. Degree of polymerization was calculated using the equations shown in Table I.

Table I. D.P. -- Viscosity Equation

Polymer	Solvent	Temp. (°C.)	Equation	Ref.
Polystyrene	Toluene	30	$1.2 \times 10^{-4}M^{0.70}$	6)
Poly(vinyl acetate)	Acetone	30	$5.02 \times 10^{-4}M^{0.62}$	7)
Poly(methyl methacrylate)	Chloroform	20	$0.485 \times 10^{-4}M^{0.80}$	8)
Polyacrylonitrile	Dimethyl-formamide	25	$1.66 \times 10^{-4}M^{0.81}$	9)

Section 3. Catalytic Activity of Di-n-butylmercury -- Metal Halide Systems for Vinyl Polymerization

Experimental results are shown in Table II on the vinyl acetate polymerization by the binary systems. As seen in Table II, $ZnCl_2$, $BiCl_3$ and $SbCl_3$ show prominent cocatalytic action. Besides these halides $SnCl_4$, $SbCl_5$, $CrCl_3$ and $TiCl_3$ are fairly effective. Examples of ineffective halides are as follows: $BeCl_2$, $MgCl_2$, $BF_3 \cdot (C_2H_5)_2O$, $PbCl_2$, PCl_3, PCl_5, $AsCl_3$, $CuCl$, $AgCl$, $CdCl_2$, Hg_2Cl_2, $HgCl_2$, $TiCl_4$, $ZrCl_4$, VCl_3, $MnCl_2$, $FeCl_3$, $CoCl_2$, $NiCl_2$, $InCl_3$, $TlCl_3$, $CeCl_3$, $ThCl_3$, $NbCl_5$, $TaCl_5$, $PdCl_2$ etc.

It was confirmed that the metal halides mentioned above by themselves did not induce high polymerization of vinyl compounds. Titanium tetrachloride apparently reacted with di-n-butylmercury; the product formed, however, had no catalytic activity. When solid halide was mixed

with dibutylmercury, there was observed no remarkable change. On the contrary, addition of di-n-butylmercury to the benzene solution of $SbCl_3$ resulted in the formation of white precipitate.

As seen in Table II, the catalytic activity varied in according to the sort of solvent. This fact may mainly be attributed to the difference of the solubility of the halide or of the reaction product in these solvents.

In contrast to the activity of zinc chloride, zinc oxide and acetate showed no cocatalytic activity.

Table II. Polymerization of Vinyl Acetate[a)]

Metal halide	Solvent (ml.)	Extent of polymerization (%)
None	Dioxane (5)	0
$ZnCl_2$	Dioxane (5)	72.8
$BiCl_3$	Dioxane (5)	80.8
$SbCl_3$	Dioxane (5)	38.9
$ZnBr_2$	Dioxane(1) + Hexane(1)	100
ZnO	Dioxane(1) + Hexane(1)	0
$Zn(OCOCH_3)_2$	Dioxane (1.5)	0
$ZnCl_2$	Ethyl acetate (3)	83.7
$ZnCl_2$	Ether (5)	16.0
$ZnCl_2$	Benzene (5)	trace
$BiCl_3$	Heptane (5)	18.2

a) Monomer, 5 ml.; $HgBu_2$ and metal halide, 1 mole % for the monomer, respectively; 15°C.; 50 hrs.

In Table III is given the examples of the result of methyl methacrylate polymerization by these binary systems. Besides the halides which are not listed in Table III, VCl_4 and $VOCl_3$ were highly active cocatalysts.

Table III. Polymerization of Methyl Methacrylate[a)]

Metal halide	Extent of polymerization(%)	Metal halide	Extent of polymerization(%)
None	0	$ZnCl_2$	87
$SnCl_4$	3.0	$TiCl_3$	18
PCl_3	47	$ZrCl_4$	21
PCl_5	4.2	VCl_3	49
$SbCl_3$	81	$CrCl_3$	63
$BiCl_3$	86	$CoCl_2$	31

a) Monomer, 3 ml.; dioxane, 1.5 ml.; di-n-butylmercury, 0.1 ml.; metal halide, equimolar to $HgBu_2$; 15°C.; 50 hrs.

Judging from Tables II and III, halides with cocatalytic activity are the compounds of zinc, IV and V group elements, and some transition metals; all of these elements having the electronegativity value from 1.5 to 2.0. The electronegativity of Hg (II) is 1.9[10)].

The binary systems of dibutylmercury and metal halide show catalytic activity also for the polymerization of vinyl monomers other than vinyl acetate and methyl methacrylate, as shown in Table IV.

Table IV. Polymerization of Various Vinyl Monomers[a)]

Monomer	Metal halide	Time	Extent of polymerization (%)		D.P.
Styrene	None	20 days	trace	----	----
Styrene	$ZnCl_2$[b)]	20 days	6.5	3.47	20200
Acrylonitrile	None	25 hrs.	0	----	----
Acrylonitrile	$ZnCl_2$	25 hrs.	0.6	----	----
Acrylonitrile	$SbCl_3$	25 hrs.	16.1	1.97	2020
Acrylonitrile	$CrCl_3$	25 hrs.	25.0	1.95	2000
Methyl acrylate	None	25 hrs.	0	----	----
Methyl acrylate	$ZnCl_2$	25 hrs.	71.9	1.63	----
Methyl acrylate	$SbCl_3$	25 hrs.	62.1	----	----
Methyl acrylate	$CrCl_3$	25 hrs.	53.9	1.14	----

a) Monomer, 2 ml.; $HgBu_2$ and metal halide, 1 mole % for the monomer, respectively; 10°C.

b) $ZnCl_2$ alone can not induce styrene polymerization.

Section 4. Effect of Inhibitor

The effect of some inhibitors for radical polymerization was studied upon the vinyl polymerization catalyzed by di-n-butylmercury -- metal halide systems. The results are summarized in Table V.

When DPPH (α,α'-diphenyl-β-picrylhydrazyl) was added to the reaction system, the color of DPPH was observed to disappear gradually. The case

was the same when $CrCl_3$ was used as halide component. Polymerization was completely suppressed as seen in Table V. Inhibitory action of p-benzoquinone was also clear, in contrast to the dialkyl-zinc or -cadmium catalyzed vinyl polymerization[11], when quinones were found to act as cocatalyst, not as inhibitor. Oxygen also inhibited the polymerization.

Table V. Effect of Inhibitors in Bu_2Hg-MX Catalyzed Polymerization of MMA[a]

MX	Inhibitor	Atmosphere	Extent of polymerization (%)	$\bar{P}$
$SbCl_3$	None	N_2	6.2	-----
$SbCl_3$	DPPH	N_2	0	-----
$ZnCl_2$	None	N_2	3.7	-----
$ZnCl_2$	DPPH	N_2	0	-----
$SbCl_3$	None	N_2	7.2	7300
$SbCl_3$	p-Benzoquinone	N_2	3.3	700
$ZnCl_2$	None	N_2	3.7	-----
$ZnCl_2$	p-Benzoquinone	N_2	0	-----
$SbCl_3$	None	N_2	6.6	11000
$SbCl_3$	None	O_2	0.7	1500
$ZnCl_2$[b]	None	N_2	25.7	-----
$ZnCl_2$	None	O_2	trace	-----

a) Bu_2Hg and MX, 1 mole % for monomer; inhibitor, 10 mole % for MX; temperature, 15°C.; time, 20 hrs.

b) 50 Hrs. Reaction.

Section 5. Copolymerization

Copolymerizations of equimolar mixture of vinyl compounds were examined using various dibutylmercury -- metal halide systems as catalyst. The results are summarized in Table VI.

Table VI. Copolymerization (Equimolar Monomer Mixture)[a)]

Monomer mixture		Metal halide	Extent of polymerization(%)	Content of monomer (1) in copolymer(%)
Monomer (1)	Monomer (2)			
Methyl methacrylate	Vinyl acetate	$ZnCl_2$	15	84.5
"	"	$CrCl_3$	28.5	78.7
Acrylonitrile	Methyl methacrylate	$ZnCl_2$	4.0	36.9
"	"	$SbCl_3$	10.8	29.8
"	"	$CrCl_3$	43.9	34.0
Methyl methacrylate	Styrene	$ZnCl_2$	14.8	56.0
"	"	$SbCl_3$[b)]	5.9	51.8
"	"	$SbCl_3$	8.5	52.2
"	"	$SbCl_3$[c)]	4.7	51.7
"	"	$BiCl_3$	7.1	58.7
"	"	$TiCl_3$	6.1	53.4
"	"	$ZrCl_4$	2.7	53.9
"	"	VCl_3	1.7	52.5
"	"	$CrCl_3$	3.9	52.8
"	"	$CoCl_2$	4.1	53.4

a) Monomer mixture, 0.05 mole; $HgBu_2$ and metal halide, 1 mole % for monomer; 15°C.
b) $SbCl_3/ HgBu_2 = 1/2$. c) $SbCl_3/ HgBu_2 = 2/1$.

Thus, copolymer composition agrees well with that of the usual radical copolymer. Table VII shows a more detailed data on methyl methacrylate -- styrene copolymerization.

Table VII. Methyl Methacrylate -- Styrene Copolymerization by $HgBu_2$ -- $ZnCl_2$ System[a)]

Monomer ratio (mole)		Extent of	Copolymer composition (%)	
Methyl methacrylate (1)	Styrene (2)	polymerization (%)	(1)	(2)
9	1	9.3	80.3	19.7
8	2	3.2	69.4	30.6
7	3	1.3	63.6	36.4
6	4	1.6	56.5	43.5
5	5	14.8	56.0	44.0
4	6	2.3	45.6	54.4
3	7	4.5	36.4	63.6
2	8	4.8	32.6	67.4

a) Monomer mixture, 0.05 mol.; $HgBu_2$ and $ZnCl_2$, 1mole % for monomer, respectively; 15 °C.

Section 6. Kinetics

Methyl methacrylate polymerization was studied in some detail, using $HgBu_2$ -- $SbCl_3$, $SbCl_3$ was used as benzene solution, to make the reaction system homogeneous.

6-1. Effect of Catalyst Concentration

In Tables VIII and IX are shown the results of methyl methacrylate polymerization, varying the concentration of one component at a constant concentration of the other component of Bu_2Hg -- $SbCl_3$ system.

Table VIII. Effect of Catalyst Concentration (I)[a)]

Bu_2Hg/monomer (%)	$SbCl_3$/monomer (%)	$Bu_2Hg/SbCl_3$	Extent of polymerization (%)	$\bar{P}$
0.4	2.0	0.2	0	----
1.0	2.0	0.5	trace	----
2.0	2.0	1.0	3.2	4700
3.0	2.0	1.5	4.7	4900
4.0	2.0	2.0	7.3	4100
6.0	2.0	3.0	10.8	3600

a) Monomer, MMA 3 ml.; solvent, benzene 3 ml.; temperature, 30°C.; time, 7 hrs.; constant concentration of $SbCl_3$.

Table IX. Effect of Catalyst Concentration (II)[a)]

Bu_2Hg/monomer (%)	$SbCl_3$/monomer (%)	$Bu_2Hg/SbCl_3$	Extent of polymerization(%)
2.0	0.5	4.0	trace
2.0	1.0	2.0	0.29
2.0	2.0	1.0	0.75
2.0	2.5	0.8	1.18

a) Monomer, MMA 3 ml.; solvent, benzene 4 ml.; temperature, 30°C.; time, 7 hrs.; constant concentration of Bu_2Hg.

There was found monotonous increase in the extent of polymerization with the increase in the concentration of each component, and no optimum ratio in catalyst components was observed. The degree of polymerization decreased with the increase in the catalyst concentration.

6-2. Temperature Dependence

The polymerization of methyl methacrylate by Bu_2Hg -- $SbCl_3$ system was studied at various temperatures, as given in Table X.

The degree of polymerization was almost constant throughout the whole reaction time except for the initial period. Reaction rate R_p at each temperature was calculated by the data given in Table X. Plotting log R_p with the reciprocal reaction temperature the over-all activation energy E_{R_p} was found to have a value 20 kcal./mole. From the relation between the degree of polymerization and the reaction temperature $E_{1/\overline{P}}$ was found to be -9 kcal/mole. Assuming that usual rate equations for radical polymerization may be applied to the relevant reaction and that any transfer reactions may be neglected, the values,

$$E_i = 29 \text{ kcal./mole}$$

$$E_p - \frac{1}{2} E_t = 5.5 \text{ kcal./mole}$$

are obtained from the apparent activation energy values cited above, where E_i, E_p and E_t imply the activation energies for initiation, propagation and termination, respectively. These values are similar to the data so far obtained for the usual radical polymerizations ($E_i = 30 \pm 1$ kcal./mole[12,13,14], $E_p - \frac{1}{2} E_t = 4.4 - 4.7$ kcal./mole[15,16]),

and may show the polymerization of methyl methacrylate by Bu_2Hg -- $SbCl_3$ system to proceed by a mechanism similar to the usual radical polymerization.

Table X. Polymerization of MMA by Bu_2Hg -- $SbCl_3$ System at Various Temperatures[a)]

Temperature (°C.)	Time (hr.)	Extent of polymerization (%)	$\bar{P}$
30	1.0	0.08	6300
30	3.0	0.31	3700
30	5.0	2.5	7300
30	6.0	3.8	8000
45	1.0	2.2	6100
45	2.0	8.4	3200
45	3.0	17.1	2400
45	4.0	27.0	1900
45	5.0	33.6	2200
45	6.0	47.6	1700
60	0.5	3.1	4400
60	1.0	9.6	2700
60	1.5	17.6	2400
60	2.0	20.1	2500
60	2.5	29.5	2600
60	4.0	37.0	2700

a) Monomer, MMA 3 ml.; solvent, benzene 1 ml.; Bu_2Hg and $SbCl_3$, 2 mole % for monomer.

Section 7. Discussion

The behavior of dibutylmercury -- metal halide systems toward some radical inhibitors, the results of kinetic and copolymerization study allow us to consider that the polymerization proceeds through a radical mechanism, independently of the kinds of metal halides in all the cases examined. This fact is in clear contrast to the olefin polymerization by Ziegler type catalyst, where 'coordinated anionic' mechanism was proposed.

Mercury alkyl(aryl) has been known to react with the halide of metal with larger electronegativity than mercury to give the organic compound of the metal, e.g.[17],

$$2(C_6H_5)_2Hg + SnCl_4 = 2C_6H_5HgCl + (C_6H_5)_2SnCl_2$$

$$2(C_6H_5)_2Hg + SbCl_3 = (C_6H_5)_3SbCl_2 + C_6H_5HgCl + Hg$$

Generally,

$$HgR_2 + MeX_n = \underset{(A)}{RHgX} + \underset{(B)}{RMeX_{n-1}} \text{ (etc.)} \qquad (1)$$

Me = B, Si, Sn, Pb, P, As, Sb, Bi.

The metal halides usually remove only one organic group (R) from the mercury. Therefore, type (B) compound, formed by the reaction of mercury alkyl with halide, may be considered to decompose radically to induce the polymerization. Type (A) compound, e.g., BuHgX, was proved to have no catalytic activity. In case of the halide of transition metal similar reaction may be probable[18]. However, as seen in Table II, Chapter 5, digested reaction product of Bu_2Hg with metal halide showed

only poor activity.

The electronegativity of zinc (1.5) is smaller than that of mercury (1.9). If reaction (2) takes place,

$$R_2Hg + ZnCl_2 \rightleftharpoons RHgCl + RZnCl \quad (2)$$

(B')

type (B) compound behaves quite differently from the Bu_2Hg -- $ZnCl_2$ system; C_2H_5ZnI can induce the polymerization of methyl methacrylate and acrylonitrile only when oxygen is present as cocatalyst.

Hence, the radical decomposition of some intermediate complex in course of reaction (1) may rather be probable, than the radical decomposition of type (B) compound.

$$R_2Hg + ZnCl_2 \longrightarrow R - Hg\begin{matrix} R \\ \diagdown\ \diagup \\ Cl \end{matrix}Zn - Cl$$

$$\longrightarrow R - Hg\cdot + R\cdot + ZnCl_2 \quad (3)$$

Similar type of the mechanism has been postulated in case of the alkylcadmium -- quinone system catalyzed polymerization[19].

Further discussions of the mechanism will be made in the next chapter, together with the cases of the systems containing other organometallic compounds than mercury alkyl.

References for Chapter 4

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CHAPTER 5

METAL ALKYL — METAL HALIDE SYSTEM

Section 1. Introduction

Among the utilization of the organometallic compound in the polymer chemistry and industry, Ziegler-Natta catalyst is the most distinguished, which consists of aluminum alkyl and titanium chloride and is excellent catalyst for the low pressure polymerization of ethylene and for the stereospecific polymerization of propylene.

Since the discovery of aluminum alkyl-titanium chloride for the olefin polymerization, many systems composed of organometallic compound and halide or other salt of the transition metal have been studied and were found to be good catalyst for ethylene- or propylene-polymerization.

'Ziegler type' catalyst, organometallic compound -- metal halide system (RM-MX), is generally considered to induce 'coordinated anionic' polymerization of olefin (1).

$$RM + M'X \longrightarrow \underset{\text{(complex)}}{RM \cdot M'X} \xrightarrow{C=C} \overset{C=C}{\underset{RM \cdot M'X}{\vdots\ \vdots}} \qquad (1)$$

However, the behavior of RM-MX system in vinyl polymerization is

rather different from type (1) and the polymerization seems to proceed through a radical mechanism in many cases. One of the examples has already been shown in the previous chapter, in case of dibutylmercury -- metal halide system.

This chapter deals with the behavior of RM-MX systems for vinyl polymerization. Discussion will also be made in connection with the coordinated anionic polymerization.

Section 2. Experimental

2-1. Material

Vinyl monomers and solvents were purified by the usual methods[1]. Glycol dimethacrylate was prepared by the acid-catalyzed transesterification of methyl methacrylate with ethylene glycol, followed by vacuum distillation[2,3]. B.p. 100 -- 105°C./ 3 mm (ref. b.p. 83 -- 85°C./ 1 mm).

Metal alkyls were prepared according to the standard methods. Metal halides used were the commercial material of the highest purity. Liquid halides were distilled if necessary.

2-2. Polymerization Procedure

Polymerization was generally carried out under an atmosphere of nitrogen in a sealed tube or in a test tube with ground-glass stopper

by keeping it to stand or rotate in a constant temperature bath. All the reactions should be conducted under nitrogen to avoid the other possible reactions caused by the oxygen cocatalysis cited in the introduction.

The order of addition of the reagents has, as mentioned later, an important factor for the catalytic activity. Reagents were mixed with one another in the order : (A), solvent-MX-monomer-RM; (B), solvent-MX-RM-monomer. In some runs of case (B) the system was digested for a while prior to the addition of monomer.

After a definite time interval, the polymerization was stopped by adding methanol containing hydrochloric acid. Polymer thus formed was separated and purified by the usual way[1]. When solid halide was used as catalyst component, polymer separated was dissolved in a suitable solvent and filtered off from solid residue. The degree of polymerization was determined by viscometry[1].

2-3. Electron Paramagnetic Resonance Study

The reaction mixture was sealed under the atmosphere of nitrogen or argon in a glass sample tube designed to fit directly into the microwave resonant cavity and the absorption was measured at room temperature or at the temperature of Dry Ice*).

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*) Electron paramagnetic resonance measurement was carried out at the laboratory of Sumitomo Electric Industries Ltd., Osaka, Japan. We are grateful to Messrs. M. Izumi and H. Shima for the use of EPR facilities of their laboratory.

Section 3. Metal Alkyl -- Metal Halide System for Vinyl Polymerization

As stated in the introduction, alkyl compounds of metals of the groups other than I_A and II_A in the periodic table have no catalytic activity for vinyl polymerization in the absence of a suitable cocatalyst.

The writer has found that some binary systems composed of metal alkyl and metal halide (in some cases, oxyhalide, nitrate or acetylacetonate) can be active initiators for vinyl polymerization. The kind of metal halide, MX, as cocatalyst depends on the nature of its partner metal alkyl, RM, monomer and solvent. Table I summarizes the results of the experiment on the catalytic activity of RM-MX system for the polymerization of some vinyl monomers.

The procedure of the preparation of the catalyst system has also a major effect upon the activity of the catalytic system (cf. Section 4).

Titanium tetrachloride, a well-known component of Ziegler catalyst, generally has a low activity for the polymerization of polar vinyl compound; on the contrary, vanadium compound, e.g., vanadium tetrachloride or vanadyl trichloride, was found to be an excellent cocatalyst in these vinyl polymerizations.

While alkyl compound of the metal of I_A or II_A group induces anionic polymerization of vinyl compound, the mixed systems of these metal alkyls with metal halides, e.g., butyllithium -- metal halide system, showed only a very poor catalytic activity. For example, there occurred no polymerization when butyllithium was mixed with titanium tetrachloride or vanadyl trichloride in the presence of vinyl monomers.

Table I. Catalytic Activity of RM-MX System for Vinyl Polymerization[a)]

RM (mole %)	MX (mole %)	b) Monomer (ml.)	Solvent (ml.)	c) Mixing order	Temp. (°C.)	Time (hr.)	Extent of polym'n (%)	Ref. and Note
Et_2Zn(2)	----	MMA(5)	Hexane(5)	----	20	24	2	
"	$HgCl_2$(1)	"	"	A	20	24	47	
"	PCl_5	"	"	A	20	24	50	
"	$VOCl_3$	"	"	A	20	24	82	d)
"	VCl_4	"	"	A	20	24	66	
"	VCl_3	"	Dioxane(5)	A	20	24	52	
"	$FeCl_3$	"	"	A	20	24	90	
"	----	VAc(5)	----	---	20	24	0	
"	$VOCl_3$	"	----	A	20	24	49	
"	VCl_4	"	----	A	20	24	56	
Et_2Cd(2)	----	MMA(5)	Heptane(5)	B	20	20	10	
"	$MgBr_2$	"	"	B	20	20	33	
"	$CdBr_2$	"	"	B	20	20	27	
"	$FeCl_3$	"	"	B	20	20	50	e)
"	$NiCl_2$	"	"	B	20	20	39	
"	$VOCl_3$	"	"	B	20	20	37	
"	$PtCl_2$	"	"	B	20	20	60	
"	----	VAc(5)	----	---	20	20	0	
"	$VOCl_3$	VAc(3)	Dioxane(5)	A	20	21	34	
"	VCl_4	"	"	A	20	27	39	
Bu_2Hg	----	MMA(3)	Dioxane(1.5)	---	15	50	0	
"	PCl_3(1)	"	"	A	15	50	47	
"	$SbCl_3$	"	"	A	15	50	81	
"	$BiCl_3$	"	"	A	15	50	86	
"	$ZnCl_2$	"	"	A	15	50	87	4)
"	VCl_3	"	"	A	15	50	49	
"	$CrCl_3$	"	"	A	15	50	63	
"	$VOCl_3$	"	"	A	20	30	84	
"	VCl_4	"	"	A	20	30	52	
"	VCl_4	VAc(3)	"	A	20	30	0	
Bu_3B(2)	----	VAc(5)	Dioxane(5)	---	20	18	8	f)
"	$BF_3 \cdot Et_2O$(2)	"	"	A	20	18	23	
"	----	MMA(5)	Xylene(5)	---	60	3	50	
"	$BF_3 \cdot Et_2O$(2)	"	"	B	60	3	16	5)
"	----	AN(5)	"	---	60	3	3	
"	$BF_3 \cdot Et_2O$(2)	"	"	B	60	3	15	

(continued)

RM (mole %)	MX (mole %)	b) Monomer (ml.)	Solvent (ml.)	c) Mixing order	Temp. (°C.)	Time (hr.)	Extent of polym'n (%)	Ref. and Note
Et_3Al(2)	----	VAc(5)	Dioxane(5)	---	20	40	4	
"	$BF_3 \cdot Et_2O$(1)	"	"	A	20	40	37	f)
"	VCl_4(1)	"	"	A	20	40	36	f)
"	$VOCl_3$(2)	"	"	A	20	40	18	f)
Pr_4Sn(2)	----	MMA(5)	----	---	20	40	0	
"	$TiCl_4$(1)	"	----	A	20	40	0	
"	$VOCl_3$	"	----	A	20	40	0	
"	$VOCl_3$	VAc(5)	Dioxane(5)	A	20	40	0	f)
Et_4Pb(2)	----	MMA(3)	Heptane(5)	---	20	24	0	
"	$ZnCl_2$(1)	"	Heptane(3) Dioxane(1)	B	20	37	44	6)
"	$AlCl_3$	"	"	B	20	37	43	6)
"	$TiCl_3$	"	"	B	20	37	26	6)
"	$ZrCl_4$	"	"	B	20	37	53	6)
"	$BiCl_3$	"	"	B	20	37	56	6)
"	VCl_3	"	"	B	20	37	25	6)
"	VCl_4	"	"	B	20	37	80	6)
"	$VOCl_2$	"	"	B	20	37	77	6)
Et_3P(2)	----	MMA(5)	Hexane(15)	---	20	18	Oily polymer	
"	$TiCl_4$(1)	"	"	B	20	18	0	7)
"	----	VAc(5)	"	---	20	18	0	7)
"	$TiCl_4$	"	"	B	20	18	0	7)
Et_3Sb(2)	----	MMA(3)	----	---	20	20	0	
"	$VOCl_3$(1)	"	----	A	20	20	1	
"	$TiCl_4$	"	----	A	20	20	0	
Et_3Bi(2)	----	MMA(3)	----	---	20	20	0	
"	$VOCl_3$(1)	"	----	A	20	20	59	
"	$TiCl_4$	"	----	A	20	20	1	
Et_2Se(2)	----	MMA(3)	Hexane(3)	---	20	240	0	
"	$BF_3 \cdot Et_2O$(1)	"	Hexane(1) Tetrahydrofuran(2)	B	20	240	50	g)
"	HgCl	"	"	B	20	240	10	g)

a) Reaction under nitrogen atmosphere. b) MMA: Methyl methacrylate; VAc: Vinyl acetate; AN: Acrylonitrile. c) A: Solvent-MX-monomer-RM; B: Solvent-MX-RM-monomer. d) Experiment by Yukio Nakayama. e) Experiment by Kazuo Ito. f) Experiment by Takanobu Imada. g) Experiment by Ryozo Sakata.

When butyllithium was mixed with I_A- and II_A-metal halides, there was observed little change in the polymerization rate, but the steric structure of the obtained polymer, e.g., poly(methyl methacrylate) was markedly varied[8]. The behaviour of magnesium alkyl is much the same as lithium alkyl.

Results of polymerization induced by the alkyl compound of the metals other than groups I_A and II_A are shown in Table I. It seems rather difficult to derive any general rule which can predict the kind of the metal halide suitable for a particular metal alkyl. Alkali and alkaline earth metal halides have no cocatalytic activity for any of the metal alkyls. On the other hand, halogen compounds of the metals with the electronegativity ranging from 1.5 to 2.0 were generally effective. The solubility of the original metal halide, MX, or of the reaction product of RM with MX may not be ignored for more quantitative consideration of the catalytic activity. The situation will rather be complicated.

Section 4. Preparation Condition of the Catalyst System and its Activity

As stated above, the preparation procedure of the catalyst, especially the order of mixing of the catalyst components, greatly affects the activity of the catalyst prepared, as shown in Table II.

Table II. Order of Mixing and Catalytic Activity[a)]

Catalyst system	Monomer (ml.)	Solvent (ml.)	Mixing order[b)]	Temp. (°C.)	Time (hr.)	Extent of polym'n. (%)	Ref.
Et_2Zn-$VOCl_3$	VAc(5)	----	A	20	24	49	
Et_2Zn-$VOCl_3$	VAc(5)	Heptane(1)	B	20	24	trace	
Et_2Zn-VCl_4	VAc(5)	----	A	20	24	56	
Et_2Zn-VCl_4	VAc(5)	Heptane(1)	B	20	24	trace	
Et_2Cd-VCl_4	VAc(5)	Hexane(5)	A	20	27	55	
Et_2Cd-VCl_4	VAc(5)	Hexane(7)	B[c)]	50	63	2	
Bu_2Hg-$ZnCl_2$[e)]	MMA(3)	Ether (2)	A	20	20	26	4)
Bu_2Hg-$ZnCl_2$	MMA(3)	Ether (2)	B[d)]	20	20	0	
Bu_2Hg-$SbCl_3$[f)]	MMA(3)	Benzene(2)	A	20	20	7	
Bu_2Hg-$SbCl_3$	MMA(3)	Benzene(2)	B[d)]	20	20	1	

a) Reaction under nitrogen atmosphere; RM and MX, 2 and 1 mole % for monomer, respectively.
b) The same notation as in Table II.
c) Digested at 50°C. for 5 hrs.
d) Digested at room temperature for 20 hrs.
e) Used as ether solution.
f) Used as benzene solution.

In order to obtain a 'homogeneous' catalyst system, liquid MX's were used as halide component in most of the experiments in Table II or later. Solid halides were used in the form of solution using a suitable solvent. It will clearly be seen in Table II, that an RM-MX system has only a poor catalytic activity when vinyl monomer is mixed with the RM-MX mixture preliminarily prepared. On the contrary, the catalytic

activity was excellent when the two components, i.e., RM and MX, were mixed in the presence of monomer.

This fact is in sharp contrast to the olefin polymerization by Ziegler type catalyst where the polymerization proceeds smoothly by RM-MX complex prelimiarily prepared.

In some cases the kind of solvent has a major influence on the activity of RM-MX system, as shown in Table III.

The effect of solvent seemed not so prominent in case of the methyl methacrylate polymerization. When a solid metal halide was mixed with metal alkyl, there was usually observed little change in the reaction system. With liquid halide as component, the situation was quite different: The components react with or without the precipitation of the reaction products. When aluminum- or mercury-alkyl was used as RM component, most of the reaction system remained homogeneous. While when zinc- or cadmium-alkyl was used, the system became heterogeneous. It is interesting that the reaction of triethylaluminum with titanium tetrachloride in the presence of polar vinyl compound results in the formation of homogeneous system, though well-known Ziegler catalyst, $Al(C_2H_5)_3$-$TiCl_4$ system in hydrocarbon, is heterogeneous.

Section 5. Copolymerization

Copolymerization of vinyl compounds was studied using various RM-MX systems as shown in Tables IV, V, VI and VII.

Table III. Effect of Solvent[a)]

RM (mole %)	MX (mole %)	Monomer (ml.)	Solvent (ml.)	Temp. (°C.)	Time (hr.)	Extent of polym'n. (%)	$\bar{P}$
Et_2Zn(2)	$VOCl_3$(1)	VAc(3)	Hexane (5)	25	17	6	100
"	"	"	Toluene	25	17	trace	---
"	"	"	Dioxane	25	17	58	70
"	"	"	Tetrahydrofuran	25	17	1	---
"	"	"	Ethyl acetate	25	17	4	30
"	"	"	None	25	20	49	---
"	"	MMA(3)	Hexane (5)	25	20	43	---
"	"	"	Toluene	25	20	56	210
"	"	"	Dioxane	25	20	18	---
"	"	"	Tetrahydrofuran	25	20	30	960
Et_2Cd(2)	$VOCl_3$(1)	VAc(3)	Hexane (5)	20	21	trace	---
"	"	"	Toluene	20	21	12	60
"	"	"	Dioxane	20	21	34	85
"	"	"	Tetrahydrofuran	20	21	4	65
"	"	"	Ethyl acetate	20	21	1	550
"	"	"	None	20	72	29	100
"	VCl_4(1)	"	Hexane (5)	20	27	55	---
"	"	"	Toluene	20	27	18	105
"	"	"	Dioxane	20	27	39	---
"	"	"	Tetrahydrofuran	20	27	8	70
"	"	"	Ethyl acetate	20	27	10	110
"	"	"	None	20	72	56	150
Bu_2Hg(2)	$VOCl_3$(3)	MMA(3)	Hexane (5)	30	20	86	---
"	"	"	Toluene	30	20	100	---
"	"	"	Dioxane	30	20	84	1170
"	"	"	Tetrahydrofuran	30	20	86	450
"	"	"	Ethyl acetate	30	20	100	---
"	VCl_4(2)	"	Hexane	30	20	52	---
"	"	"	Toluene	30	20	20	---
"	"	"	Dioxane	30	20	52	1100
"	"	"	Tetrahydrofuran	30	20	81	1200
"	"	"	Ethyl acetate	30	20	63	1250

a) Order of mixing, A.

Table IV. Copolymerization by Et_2Zn -- MX System[a)]

MX	Comonomer (1)	Comonomer (2)	Total monomer	Monomer ratio (%) (1)	Monomer ratio (%) (2)	Solvent (ml.)	Mixing order	Temp. (°C.)	Time (hr.)	(1)-Content in co-polymer (%)
$VOCl_3$	MMA	ST[b)]	3 ml.	80	20	Toluene(5)	A	50	7	72.2
"	"	"	"	50	50	"	A	50	7	48.1
"	"	"	"	20	80	"	A	50	7	28.8
"	"	"	"	80	20	THF (5)[c)]	A	50	7	75.4
"	"	"	"	50	50	THF (5)	A	50	7	50.0
"	"	"	"	20	80	"	A	50	7	26.4
"	"	"	"	80	20	Hexane(5)	A	20	24	72.1
"	"	"	"	50	50	"	A	20	24	49.3
"	"	"	"	20	80	"	A	20	24	33.0
VCl_4	"	"	"	80	20	"	A	20	24	72.6
"	"	"	"	50	50	"	A	20	24	48.9
"	"	"	"	20	80	"	A	20	24	29.1
$VOCl_3$	"	"	0.05 mol.	80	20	Dioxane(7)	A	20	20	74.9
"	"	"	"	50	50	"	A	20	20	50.7
"	"	"	"	20	80	"	A	20	20	27.5
"	"	"	"	80	20	THF (7)	A	20	20	71.5
"	"	"	"	50	50	"	A	20	20	50.2
"	"	"	"	20	80	"	A	20	20	32.9
"	"	"	"	50	50	Hexane(7)	B[d)]	60	7	56.8
"	"	"	"	50	50	Hexane(5) + Dioxane(2)	B	60	7	59.1
"	"	"	"	50	50	None	A	20	20	45.6
VCl_4	"	"	"	50	50	None	A	20	20	51.2
$VOCl_3$	VAc	ST	"	50	50	None	A	20	20	2.3
VCl_4	"	"	"	50	50	None	A	20	20	4.8
$TiCl_4$	MMA	"	"	50	50	THF (7)	A	20	20	50.5
"	"	"	"	50	50	Dioxane	A	20	20	45.0
"	"	"	"	50	50	Hexane	B[d)]	60	7	57.2
"	"	"	"	50	50	Hexane(5) + Dioxane(2)	B	60	7	50.3

a) RM, 2 mole %; MX, 1 mole % for monomer; extent of polymerization, lower than 10 %.
b) ST : Styrene. c) THF : Tetrahydrofuran.
d) Digested at 60°C. for 3 hrs.

Table V. Copolymerization by Et_2Cd -- MX System[a)]

MX	Comonomer (1)	Comonomer (2)	Monomer ratio(%) (1)	Monomer ratio(%) (2)	Solvent (ml.)	Mixing order	Temp. (°C.)	Time (hr.)	(1)-Content in co-polymer (%)
$VOCl_3$	MMA	ST	80	20	Hexane(7)	A	20	20	61.9
"	"	"	60	40	"	A	20	20	56.6
"	"	"	40	60	"	A	20	20	40.3
"	"	"	80	20	Dioxane(7)	A	20	20	70.2
"	"	"	60	40	"	A	20	20	50.0
"	"	"	20	80	"	A	20	20	25.2
"	"	"	50	50	None	A	20	21	50.6
VCl_4	"	"	50	50	None	A	20	21	49.3
"	VAc	"	40	60	Hexane(7)	A	20	3	1.3
"	"	"	20	80	"	A	20	3	6.6
"	"	"	20	80	Dioxane(7)	A	20	21	2.4
$VOCl_3$	"	"	40	60	Toluene(7)	A	20	24	0.9
"	"	"	20	80	"	A	20	24	0.8
"	"	"	50	50	THF (7)	A	20	20	4.4
"	MMA	"	50	50	Ethyl acetate(7)	A	20	20	51.9
"	"	"	50	50	Chloroform	A	20	20	50.7
"	"	"	50	50	Ether	A	20	20	49.5
"	"	"	50	50	THF	A	20	22	55.3
"	"	"	50	50	Toluene	A	20	22	48.7
"	"	"	49	51	Hexane(7)	B	50	40	66
"	"	"	49	51	Dioxane	B	50	40	59
VCl_4	"	"	49	51	Hexane(7)	B	50	40	52

a) Total monomer, 0.05 mole; other conditions, see Table IV.

Table VI. Copolymerization by Bu_2Hg -- MX System[a)]

MX	Total monomer (mole)	Monomer ratio (%) (1)	(2)	Solvent (ml.)	Temp. (°C.)	Time (hr.)	MMA-Content in copolymer (%)
$SbCl_3$[b)]	0.03	80	20	Toluene(6)	20	48	68.5
"	0.03	50	50	"	20	48	50.8
"	0.03	20	80	"	20	48	23.4
"	0.03	80	20	THF (6)	20	48	69.7
"	0.03	50	50	"	20	48	53.2
"	0.03	20	80	"	20	48	24.7
$ZnCl_2$[c)]	0.03	80	20	Toluene(5) THF (1)	20	48	72.4
"	0.03	50	50	"	20	48	52.9
"	0.03	20	80	"	20	48	25.1
"	0.03	80	20	"	60	7	72.2
"	0.03	50	50	"	60	7	50.8
"	0.03	20	80	"	60	7	24.5
$VOCl_3$	0.03	80	20	Toluene(5) Heptane(1)	60	7	70.0
"	0.03	50	50	"	60	7	55.3
"	0.03	20	80	"	60	7	27.2
"	0.03	80	20	THF (5) Heptane(1)	60	7	72.8
"	0.03	50	50	"	60	7	53.4
"	0.03	20	80	"	60	7	27.6
$VOCl_3$	0.05	80	20	Toluene(7)	20	46	70.3
"	0.05	50	50	"	20	46	49.1
"	0.05	20	80	"	20	46	28.7
"	0.05	80	20	THF (7)	20	46	73.8
"	0.05	50	50	"	20	46	50.5
"	0.05	20	80	"	20	46	31.2

a) Comonomer, MMA-ST; mixing order, A; other conditions, see Table IV.

b) Used as benzene solution.

c) Used as ether solution.

Table VII. Copolymerization by other RM -- MX Systems[a)]

RM	MX	Solvent (ml.)	Mixing order	Temp. (°C.)	Time (hr.)	MMA-Content in copolymer (%)
Et_3Al	$TiCl_4$	THF (7)	A	20	50	49.3
"	"	Dioxane(7)	A	20	50	49
"	$VOCl_3$	Toluene(7)	A	20	50	51.7
"	"	Ether (7)	A	20	50	49.5
"	"	Hexane (7)	A	20	50	54
"	"	Dioxane(7)	A	20	50	53
"	VCl_4	Dioxane(7)	A	20	50	50
"	$VOCl_3$	Hexane (7)	B[b)]	50	36	49
"	"	Hexane (7) Dioxane(1)	B	50	20	55
"	$TiCl_4$	Dioxane(7)	B	50	36	50
Et_3Sb	$VOCl_3$	None	A	20	50	48.3
Et_3Bi	"	None	A	20	50	49.7

a) Comonomer, MMA-ST (1/1 mole ratio); total, 0.05 mole; other conditions, see Table IV.

b) Digested at 60°C. for 6 hrs.

Table VIII. Effect of Solvent in Copolymerization[a)]

RM	MX	Solvent (ml.) THF	Toluene	Time (hrs.)	MMA-Content in copolymer (%)
Et_2Cd	$VOCl_3$	8	0	22	55
"	"	6	2	22	56
"	"	4	4	22	42
"	"	2	6	22	52
"	"	0	8	22	49
Et_3Al	$VOCl_3$	8	0	16	--
"	"	6	2	16	57
"	"	4	4	16	55
"	"	2	6	16	48
"	"	0	8	16	51
"	VCl_4	8	0	47	53
"	"	6	2	47	53
"	"	4	4	47	50
"	"	2	6	47	51
"	$TiCl_4$	8	0	46	53
"	"	6	2	46	--
"	"	4	4	46	56
"	"	2	6	46	51
"	"	0	8	46	51

a) Comonomer, MMA-ST (1/1 mole ratio), Total, 0.05 mole; temperature, 20°C.; mixing order A; other conditions, see Table IV.

In almost all the cases examined, the catalyst components were mixed in the presence of monomer. Results obtained have shown that copolymers have much the same composition as the ordinary 'radical' copolymer irrespective of the kind of RM and MX components in the catalyst used.

The properties, e. g., polarity, of solvent used in the copolymerization reaction had no prominent effect on the composition of copolymers formed, as shown in Tables IV, V, VI, VII and VIII, under the conditions examined.

Aluminum triethyl-titanium tetrachloride system, typical Ziegler type catalyst, also gave a 'radical' type copolymer.

Section 6. Electron Paramagnetic Resonance Study

To make the mechanism of vinyl polymerization by RM -- MX system clearer, the electron paramagnetic resonance absorption of the polymerization system was studied. The halides of non-transition metal were used as MX component, for some halides of transition metal, e. g., $VOCl_3$, show absorption signals by themselves when dissolved in methyl methacrylate or tetrahydrofuran; VO^{++} and V^{4+} have been known to show absorption signals[9,10]. In the polymerizing system of methyl methacrylate (or methyl methacrylate -- styrene mixture) by any of the RM -- MX systems examined, there were observed no signals of EPR absorp-

tion spectrum at the temperature of Dry Ice.

The signals, however, were observed in the gelified polymers of glycol dimethacrylate, prepared by the relevant RM -- MX systems. The systems examined are : $Zn(C_2H_5)_2$-$HgCl_2$, $Cd(C_2H_5)_2$-$HgCl_2$, $Hg(C_4H_9)_2$-$SbCl_3$ and $Hg(C_4H_9)_2$-$ZnCl_2$, all of which had excellent catalytic activity and showed absorption signals though they were not well-defined enough to account for the detailed structure of the present radical. The spectra, however, were almost similar to that of the 'radical' polymer (prepared using α,α'-azo-bis-isobutyronitrile as initiator at 60°C.), in all the cases examined; the spectrum spreads over a region of about 100 gauss centered about a value of the magnetic field close to the position expected for a free electron, and is similar in its essential details to the spectrum previously reported by Fraenkel[11]. On the other hand, the polymer of glycol dimethacrylate prepared by butyl-lithium, an anionic catalyst, showed no absorption signals.

Section 7. Discussion

Judging from the results of copolymerization study, vinyl polymerization by RM -- MX systems may be considered to proceed by radical mechanism in almost all the cases examined. In connection with this experiment, it will be referred that Baker[12] found radical type monomer reactivity ratios in the copolymerization of vinyl chloride and vinyl

acetate by $Al(i\text{-}C_4H_9)_3$ -- $VOCl_3$ system. The behaviour of RM -- MX systems toward some radical inhibitors, the results of kinetic study (Chapter 4), and the EPR evidence in the polymerization process also lead us to the conclusion that the polymerization proceeds through a radical mechanism. This fact is in clear contrast to the olefin polymerization by Ziegler type catalyst, where 'coordinated anionic' mechanism was proposed.

As frequently mentioned in case of Ziegler type catalyst, metal alkyl RM reacts with suitable metal halide M'X to form complex. Exchange reaction of R and X between these components or the reduction of M'X by RM (to lower valence compound or to the metal) may also occur. For example, as cited in the previous chapter, mercury diaryl was known to react with some halides as follows[13]:

$$2(C_6H_5)_2Hg + SnCl_4 \longrightarrow 2C_6H_5HgCl + (C_6H_5)_2SnCl_2$$

$$2(C_6H_5)_2Hg + SbCl_3 \longrightarrow (C_6H_5)_3SbCl_2 + C_6H_5HgCl + Hg\ .$$

Reaction may generally be formulated as (2):

$$RM + M'X \longrightarrow \underset{(I)}{(RM \cdot M'X)} \longrightarrow \underset{(II)}{RMX} + \underset{(III)}{RM'X} \qquad (2)$$

As described in 3.2, the reaction product of RM with MX, such as (I), (II) or (III), has little catalytic activity for vinyl polymerization. Compounds of type (II), for example, butylmercury chloride (C_4H_9HgCl) and ethylzinc iodide (C_2H_5ZnI) were proved to exhibit no catalytic activity (Chapter 4).

Therefore, radical decomposition of the reaction product ((I), (II)

or (III)), may be eliminated from the possible initiation mechanisms. The alternate probable mechanism is a two-centered reaction in which alkyl radical is exchanged homolytically with a halogen atom through intermediate complex.

$$RM + M'X \longrightarrow R\begin{matrix}M\\M'\end{matrix}X \longrightarrow RM' + MX \qquad (3)$$

If the exchange reaction takes place in the presence of a vinyl monomer, migrating R radical may induce the polymerization.

In some cases deviations of composition from that of 'radical' copolymer were observed[14,15], which may be accounted for at least partly in terms of the heterogeneity of the reaction system.

As stated in Section 3, the kind of effective MX is varied according to the kind of RM; in general, however, the halides of metals with the electronegativity ranging from 1.5 -- 2.0 have excellent cocatalytic activity. The activity may be correlated with the easiness of homolytic reaction (3) in the presence of vinyl compound and of the attack of R radical to the coexisting monomer. The range of the electronegativity may be a measure of these conditions.

All samples of poly(methyl methacrylate) prepared by the relevant procedure were amorphous and had similar infrared spectrum to that of the usual radical polymer. It was reported that the admixing of $TiCl_4$ with $Al(C_2H_5)_3$ in the presence of styrene resulted in rapid polymerization of the monomer and formation of amorphous polystyrene[16], though $TiCl_4$ -- $Al(C_2H_5)_3$ complex preliminarily prepared was well known to

produce the isotactic polystyrene. This fact may be considered to advance clearly the dual character of the RX -- RM system : 'coordinated anionic' olefin polymerization and radical type vinyl polymerization. The former is relatively slow reaction which proceeds stereospecifically on the surface of the RM -- MX complex. When polar vinyl monomer is added to the complex, the reaction of the functional group of the monomer may be predominant and polymerization hardly takes place. On the other hand, the radical type polymerization is rather rapid reaction caused by homolytic exchange reaction between RM and M'X in the presence of monomer, and is non-stereospecific.

It is well-known that non-stereospecific polymer is also obtained in the olefin polymerization by RM -- M'X complex, and this fact may be accounted for by the incomplete regularity of structure of the catalyst complex. Some discussions will be made in the later part of this paper.

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C H A P T E R 6

MISCELLANEOUS ORGANOMETALLIC COMPOUNDS

Section 1. Introduction

In this chapter, the results of the polymerization experiment using organometallics as catalyst, which are not described in the previous chapters, are presented. They include the alkyl compounds of barium, zinc, tin, phosphor and bismuth. These results will supply the informations for the general survey of the catalytic activity of organometallic compound, which will be made in the next chapter.

Section 2. Experimental

Preparation and purification of monomers, solvents, organometallics and other commonly used materials have already been mentioned in the previous chapters. Here will be mentioned the methods of preparation etc. of the other materials than described previously.

Acrolein of the commercial material was used without further purification.

Organobarium compound, $BaZn(C_2H_5)_4$, was prepared by the same way as calcium compound, starting from barium metal and diethylzinc[1].

Diethylzinc was prepared from alkyl halide and zinc-copper couple[2]. Maximum yield 55 %, b.p. 112 -- 115°C. (ref., b.p. 115 -- 120°C.).

Tetraethyltin was prepared by the reaction of ethylmagnesium bromide with tin tetrachloride[3]. Maximum yield 60 %, b.p. 96°C./ 30 mmHg. (ref., 175°C./ 760 mmHg.).

Triethylphosphor was prepared by the reaction of ethylmagnesium bromide with phosphor tribromide[4]. Yield 40 %, b.p. 127°C. (ref., 137.5°C./ 744 mmHg.).

Trimethylbismuth was prepared from methylmagnesium iodide with bismuth trichloride[5]. Yield was not good (about 15 %) on account of poor solubility of $BiCl_3$ in ether; b.p. 105°C. (ref., 110°C.).

Polymerization process, separation and purification of polymer, and molecular weight determination were carried out by much the same procedure as described in the previous chapters.

Section 3. Organobarium Compound

As seen in Table I, similar reaction to organocalcium compound (cf. Chapter 2) was observed in case of organobarium compound, $BaZn(C_2H_5)_4$.

Poly(methyl methacrylate) by this catalyst was proved to be

crystallizable, as in the case of organocalcium catalyst.

Table I. Vinyl Polymerization Catalyzed by $BaZn(C_2H_5)_4$ [a)]

Monomer	Conversion (%)	D.P.	Note
Methyl methacrylate	26.1	2700	Polymer, insoluble in acetone
Acrylonitrile	33.5	110	
Styrene	53.4	490	
Methyl acrylate	Little	----	
Vinyl acetate	0	----	
Acrolein	Fairly high	----	Hard insoluble polymer
i-Butyl vinyl ether	0	----	

a) Monomer, 5 ml.; hexane, 10 ml.; catalyst, 1 mole %; 20°C.; 20 hrs., under N_2.

Section 4. Diethylzinc

Table II shows the results of polymerization catalyzed by diethylzinc.

In the absence of oxygen, diethylzinc showed very poor activity as polymerization catalyst. However, cocatalytic action of oxygen is apparently observed in case of vinyl acetate and styrene. Such a behavior of oxygen was observed in the boron alkyl-catalyzed polymerization, which was described in Chapter 1 of this paper. Zinc oxide,

however, had no codatalytic effect. The cocatalytic action of oxygen in these polymerizations were studied in some detail by Yukio Nakayama[6], of which will be made some discussions in later part of this chapter.

Table II. Vinyl Polymerization Catalyzed by Diethylzinc[a]

Monomer	(ml.)	Atmosphere	Yield (g.)	Conversion (%)	D.P.
Methyl methacrylate	5	N_2	2.66	55.5	326
Vinyl acetate	5	N_2	Very poor	----	---
Vinyl acetate	5	Air	0.017	0.4	---
Vinyl chloride	20[b]	N_2	0	----	---
Styrene	5	N_2	0	----	---
Styrene	5	Air	Poor	----	---
Styrene	5	N_2[c]	0	----	---
Styrene	10	d)	1.485	17	339

a) With 10 ml. of hexane as diluent, 4 days' reaction at 30°C., catalyst, 5 % for monomer.

b) 5 Hrs.' reaction at -40°C.

c) Zinc oxide (20 mole % for diethylzinc) was added to the reaction mixture.

d) N_2, 15 days, air, 10 days.

Section 5. Tetraethyltin

To 5 ml. of monomer such as acrylonitrile, methyl methacrylate, vinyl acetate, styrene or n-butyl vinyl ether in 15 ml. of hexane was

added 1 ml. of tetraethyltin, no polymerization was observed in 18 hrs. at 25°C. in every case mentioned above.

Section 6. Triethylphosphor

Horner and his coworkers[7] have studied the reactivity of the compound as polymerization catalyst. The writer carried out a qualitative experiment to compare the reactivity of the compound with that of the other organometallics. Results are shown in Table III.

Table III. Reaction of Vinyl Compounds with Triethylphosphor[a]

Monomer	Catalyst (2 mole %)	Reaction
Methyl methacrylate	$P(C_2H_5)_3$	No heat evolution, colorless liquid polymer after a night
Methyl acrylate	$P(C_2H_5)_3$	No change
Methyl methacrylate	$P(C_2H_5)_3 + B(C_2H_5)_3$	White polymer with heat evolution
Methyl methacrylate	$P(C_2H_5)_3 + TiCl_4$	No change
Vinyl acetate	$P(C_2H_5)_3$	No change
Vinyl acetate	$P(C_2H_5)_3 + B(C_2H_5)_3$	Polymer with heat evolution
Vinyl acetate	$P(C_2H_5)_3 + TiCl_4$	No change
Acrylonitrile	$P(C_2H_5)_3$	Dark brownish oily polymer with heat evolution
Acrolein	$P(C_2H_5)_3$	Yellowish brown solid by violent reaction

a) Monomer, 5 ml.; n-hexane, 15 ml.; catalyst was added under N_2-stream; reaction temp., 20°C.; reaction time 18 hrs.

The reactivity of triethylphosphor was found to be rather small, methyl methacrylate only was polymerized to form a small amount of colorless liquid polymer. In case of acrolein the reaction proceeded violently, and yellowish brown solid was formed. Acrylonitrile gave under heat evolution an oily polymer of dark brown color, which was insoluble in hexane.

Titanium tetrachloride had no cocatalytic activity with triethylphosphor. Furthermore, when triethylphosphor was added to triethylboron, the latter was found to react independently of the former.

Horner[7] explained the reactivity of triethylphosphor as a polymerization catalyst in terms of an anionic mechanism :

$$H_2C=CHX \xrightarrow{PR_3} \begin{matrix} H_2C - C^- HX \\ | \\ P^+R_3 \end{matrix}$$

On the other hand, amine is known to form a salt with alkylboron. The writer actually utilized this property to stop the alkylboron catalyzed polymerization (Chapter 1). It seems interesting that phosphine shows no inhibitory action on the trialkylboron catalyst, in contrast to amine, although phosphine and amine have a similar outerelectron configuration.

Section 7. Trimethylbismuth

A 5 ml. sample of monomer was diluted in 15 ml. of hexane, 0.5 ml. of trimethylbismuth was added and was allowed to stand for 15 hours at

30°C. under nitrogen atmosphere. Monomers such as acrylonitrile, methyl methacrylate, vinyl acetate, styrene and n-butyl vinyl ether were tested, but only acrylonitrile (yield 1.5 %) and methyl methacrylate (19.3 %) gave polymer.

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C H A P T E R 7

REACTIVITY OF ORGANOMETALLIC COMPOUND AS CATALYST FOR VINYL POLYMERIZATION

Section 1. Introduction

As frequently mentioned in the previous chapters, there appeared recently a large number of investigations on the property of organometallic compound as catalyst for the polymerization of various monomers: Not only the compounds with carbon-carbon double bond, that is, olefin, diolefin and vinyl compound, but also olefin oxide and aldehyde.

In this chapter, the writer wishes to survey the outline of the experimental results described in the previous chapters and to advance a general view on the vinyl polymerization by organometallic compounds from a standpoint of the position of metallic elements in the periodic table as well as the reactivity of the monomer molecules.

The writer and the collaborators once made such a survey of the catalytic activity of organometallic compound in one of the published papers [1]. However, the experimental data accumulated since claim an entirely renewed view on this problem.

Section 2. General Reactivity of Organometallic Compound

Organometallic compound, compound with metal-carbon bond, is generally very reactive. Many organometallics are very sensitive to air, some of them being spontaneously inflammable. They usually are thermally unstable. However, there is no parallel relation between the 'reactivity' and thermal instability or inflammability. Thermally unstable mercury- and lead-alkyls are rather poor in chemical reactivity. The reactivity is most suitably characterized by the addition reaction of organometallics to carbonyl or cyano group, as intensively studied by Gilman[2]. The reactivity was found to be closely related to the ionic-covalent nature of metal-carbon bond of the organometallics, i. e.. the electronegativity of the metal. Table I gives the relation between the reactivity in some reactions of organometallic compound and electronegativity of the metal atom. Carbon-metal bond in the Group Ia and IIa of the periodic table is considered to be principally ionic in nature. In cases of the other elements the bond is of principally covalent nature. Transition metal forms no definite metal-carbon bond except for a few cases.

The characters mentioned above are also observed in case of the organometallic-catalyzed polymerization reactions, as described in the previous chapters and will be discussed in this chapter. Of course, however, various reactivities of different organometallics in polymerization reaction as well as other reactions can not be explained only in terms of electronegativity. The difference between boron and mercury,

with much the same electronegativity, is quite distinguishable. Consideration will require many other factors.

Following sections will present arranged results on the organometallic-catalyzed polymerization according to the periodic table.

Table I. Reactivity of Metal Alkyl[a),3)]

Reaction with	Electronegativity χ	Metal	
		Reaction	No reaction
Ethers	0.9	Na	Ba
$(C_6H_5)_2$-C=CH_2	1.1	Ca	Mg
CO_2	1.5	Be, Al	Zn, Cd
R - C≡N	1.55	Zn, Cd (slow)	
RCOCl	1.7	Ga, In	Hg, Tl, B
H_2O	1.7	Ga, In	Hg, Tl, B

a) Methyl and ethyl derivatives.

Section 3. Group Ia Element (K, Na, Li; electronegativity χ = 0.8--1.0)

Organometallic compound of alkali metal, with the lowest electronegativity value (0.8 -- 1.0), shows too strong reactivity to induce moderate polymerization of polar vinyl monomers at room temperature and explosive reaction accompanying side reactions in the functional group of the monomer takes place[4)]. On the other hand organoalkali compound is a moderate catalyst for the polymerization of non-polar

monomers such as styrene[5,6], butadiene, isoprene[7,8,9] or ethylene[10]. Polar vinyl compounds, however, also give high polymer by organometallic compound of alkali by the reaction at lower temperatures, e. g., the temperature of Dry Ice.

The ionic property of carbon-alkali metal bond of these organometallics is very large and anionic mechanism in organoalkali-catalyzed polymerization was postulated[11].

The writer studied the behaviour of metal ketyl, mono- or di-alkali complex of unenolizable ketone, and considered the polymerization by metal ketyl to proceed also by an anionic mechanism (Chapter 3).

One of the distinguished features of organoalkali-catalyzed polymerization is the formation of stereospecific polymer of some monomers.

There is a well-known 'Alfin' catalyst system[5] containing organosodium compound as a component, which is very effective for the styrene polymerization and gives isotactic polystyrene. Besides Alfin catalyst, metallic lithium or its organic compound was proved to be a stereospecific catalyst for the polymerizations of isoprene[12] and some acrylic esters[6] and amides[13]. The writer also has suggested in the previous chapter the formation of stereospecific poly(methyl methacrylate) by some metal ketyls as catalyst.

The formation of 'living polymer' is another interesting nature observed in anionic polymerization. Living polymer has been observed for the first time in sodium naphthalenide catalyzed polymerization of styrene in which case an electron transfer type initiation was proposed[14].

The writer also found the formation of living polymer by di-alkali complex of unenolizable ketones (Chapter 3). Even in case of the ordinary anionic polymerizations, not electron transfer type, the formation of living polymer was observed under conditions where termination reactions are mostly eliminated, e. g., at low temperature[15].

The degree of stereospecificity of the polymerization reaction catalyzed by organoalkali-metal compounds is significantly influenced by the sort of the metal; potassium, sodium and lithium. Among these, lithium compound is the best as a stereospecific catalyst[16]. This fact may be due to the higher electronegativity and increasing covalent nature of carbon-metal bond compared with the other two metals. Lithium is said to have much more p-character than the others, which implies directional nature of the lithium-carbon bond and may be the reason of the stereospecificity of the organolithium-catalyzed polymerization reaction.

In case of the polymerization of monomers with α,β-unsaturated carbonyl system, e. g., methyl methacrylate as described in Chapter 3, it may be quite reasonable, considering many organic reactions so far studied concerning to the organometallics, to assume the initiation and propagation reactions in organometallics-catalyzed anionic polymerization to proceed by the 1,4-addition of the organometallics to the α,β-unsaturated carbonyl system. Stereoregular polymerization may be explained by specific orientation of the monomer to the polymer end in 1,4-addition propagation reaction. In this situation lithium metal may play an important role for the specific fixing of the intermediate

structure of polymer end[17]. In fact there are many stereospecific organic reactions in which organolithium compound takes part, where lithium metal is considered to take intermediately trivalent state. This is not the case for organometallic compounds of sodium and potassium.

Neverthless, in some cases stereospecific polymers were obtained by organo-sodium or -potassium catalyst[18] and the situation may rather be complicated.

When organo-sodium and -potassium compounds are used in admixture with transition metal halide (Ziegler type), the complex formed is fair catalyst for the olefin polymerization. However, the mixture can be an excellent stereospecific catalyst when lithium compound is employed as organometallic component[19]. The fact may also be accounted for partly by the reason mentioned above. Another important factor which must be taken into account is smaller ionic radius of lithium than the other alkalis; in the former the organometallics-halide complex may probably be formed more regularly than the latter cases.

Besides, it should be noted that organolithium compound, typical anionic catalyst as mentioned above, is also capable of initiating radical polymerization when oxygen effects as cocatalyst, just as in the cases of organoboron- or organozinc-catalyzed polymerization[20].

Section 4. Group IIa Element (Ca, Sr, Ba, χ = 0.9--1.0; Mg, χ = 1.2; Be, χ = 1.5)

Organoalkaline earth compounds, in the form of complex $MZnR_4$, were examined by the writer and were found to behave as polymerization catalyst much the same as organoalkali compounds (Chapter 2). Polystyrene and poly(methyl methacrylate) obtained by these compounds as catalyst were proved to be crystallizable polymer. Polyacrylates[21], poly(thiol acrylates)[22] and poly(methyl vinyl ketone)[49] of crystallizable nature were also obtained by organostrontium compound of this type. In acrylate polymerization catalysts of this type is superior in their stereospecificity than organo-lithium- or -magnesium-catalyst, maybe because of their heterogeneity. Organo-alkaline earth compound also shows very high reactivity and even methyl acrylate was not polymerized at room temperature, probably because of the reaction of the compound with the functional group of the monomer.

The mechanism of the organocalcium compound catalyzed polymerization was investigated and anionic mechanism was proposed.

As to organomagnesium compound, alkylmagnesium was utilized for the polymerization of ethylene by itself or in admixture with some transition metal compounds[23]. Dialkylmagnesium or alkylmagnesium halide, Grignard reagent, is an excellent catalyst for the polymerization of methacrylates and acrylates[24,25,26], giving stereospecific polymer, just as organolithium compound. This fact again reminds us of many specific reactions of Grignard reagents so far studied.

There are few detailed reports on organoberyllium compound as

polymerization catalyst. Alkylberyllium was used as catalyst for ethylene polymerization by itself or as mixed catalyst[27]. It was reported that in the copolymerization of vinyl monomers alkylberyllium gave copolymer of similar composition to that by alkali-, alkaline earth- or magnesium-alkyl-catalyzed copolymerization[28]; by this observation alkylberyllium may be considered to induce anionic polymerization of vinyl compounds, quite similarly to the organic compounds of the other metals of Group IIa, in spite of the larger electronegativity of beryllium.

Section 5. Group IIIa Element (B, $\chi = 1.9$; Al, $\chi = 1.5$; Ga, $\chi = 1.6$; In, $\chi = 1.5$)

Organoaluminum compound as polymerization catalyst is the most widely known in this field. However, trialkylaluminum itself gives only low polymer of ethylene. Organoaluminum compound was found also inactive as vinyl polymerization catalyst, unless some cocatalysts were used in admixture with it[29]. On the other hand, catalytic action of alkylaluminum-titanium halide complex was found by Ziegler, and has been used for the low pressure polymerization of ethylene, and stereospecific polymerization of propylene or styrene.

Alkylgallium and alkylindium were reported to induce the polymerization of ethylene to form soft, waxy polymer[27].

Organic compound of boron, which has rather large electronegativity value, was found to be quite inert to olefins, diolefins and polar

vinyl compounds. Even when boron alkyl was used in admixture with transition metal halide, the system formed had no catalytic activity for the polymerization of olefins[30] in contrast to the others of this group: Aluminum, gallium and indium.

On the other hand, trialkylboron was found to be excellent catalyst for vinyl polymerization, when molecular oxygen or other oxygen-containing compounds were present as cocatalyst. Trialkylboron-catalyzed polymerization was described in Chapter 1 in some detail. The initation reaction in this case has been explained in terms of an intermediate organometallic peroxide radical, e. g.,

$$R_3B + O_2 \longrightarrow R_2BOOR \longrightarrow R_2BO\cdot + \cdot OR$$

$$RO\cdot + CH_2{=}CHX \longrightarrow RO\text{-}CH_2\text{-}CHX\cdot .$$

Trialkylaluminum was also found to induce 'organometallic peroxide induced' radical polymerization of vinyl monomers, when molecular oxygen etc. are present as cocatalyst in the reaction system.

As frequently pointed out, the Ziegler-type catalyzed olefin polymerization has been considered to proceed by a 'coordinated anionic' mechanism. One of many speculations about the nature of Ziegler catalyst proposed the initiation by 'anionic' fission of alkyl-aluminum bond of the organoaluminum -- titanium halide complex[19].

Therefore, it should be noted that there are quite different ways of reaction of aluminum alkyl, depending upon the reaction condition and monomer employed.

Section 6. Group IVa Element (Sn, $\chi = 1.9$; Pb, $\chi = 2.1$)

As shown in the previous chapter, tetraethyltin and tetrapropyltin had no activity as polymerization catalyst for polar vinyl monomers.

Tetraethyllead was reported to polymerize some vinyl monomers as vinyl acetate[31]. This compound has recently been studied by Y. Takeda[32] and was found to be inactive in the dark. Under indoor light polymerization was observed, which may be induced by the radical decomposition of weak carbon-lead bond of the lead alkyl.

The difference between lead and tin are quite prominent, consiering that they belong to the same group of the periodic table. Carbon-tin bond strength in tetraethyltin is 45 kcal./mole and distinguishably larger than the other cases, as seen in Table II.

Table II. Strength of some Bonds[33]

Bond	Strength (kcal./mole)
Sn - H	74 a)
Pb - H	42 a)
Cd - H	19 b)
Hg - C	15 b)
Sn - C	45 b)

a) Bond energy. b) Dissociation energy.

This may account for the inactivity of organotin compound.

Even when tetraalkyltin was used as mixed catalyst with some metal halides, no catalytic activity was observed for the polymeri-

zation of vinyl compounds (Chapter 5, Table II). On the other hand tetraethyllead in combination with some metal halides, including those of non-transition metals, also was found to be effective catalyst for vinyl polymerization[32].

Concerning to this, some systems of this type containing tin- or lead-alkyl as a component are known to be catalysts for low pressure polymerization of ethylene, in which case mechanism may be somewhat different from vinyl polymerization by similar systems. In the latter case the polymerization seems to proceed by a radical mechanism.

Molecular oxygen or other oxygen-containing compounds showed no cocatalytic action on the tin- or lead-alkyl catalyzed vinyl polymerization, quite differently from the case of group IIIa elements.

Section 7. Group Va Element (P, $\chi = 3.5$; As, $\chi = 2.0$; Sb, $\chi = 1.9$; Bi, $\chi = 1.8$)

Trialkylphosphor can induce the polymerization of some vinyl monomers. However, there were obtained polymers with very low degree of polymerization, as studied by Horner[34] and described in the previous chapter. An anionic mechanism of the polymerization was proposed.

Alkylantimony also is a catalyst for the polymerization of vinyl monomers, though it shows rather low catalytic activity[1,29]. Alkylbismuth is a little more effective polymerization catalyst than antimony compounds[1]. Trialkylarsenic was reported to be used as

polymerization catalyst of α-(trifluoromethyl)acrylonitrile[35].

Titanium tetrachloride was found to show no cocatalytic activity in alkylantimony-catalyzed vinyl polymerization[1]. Some of the other metal halides, however, showed cocatalytic activity in antimony- or bismuth-alkyl catalyzed polymerization (Chapter 5, Table II).

Oxygen had cocatalytic effect on antimony- or bismuth-alkyl catalyzed vinyl polymerization, as in the case of alkylboron.

Section 8. Group Ib Element (Cu, Ag)

Organometallic compounds of the group Ib element has not been isolated. Some systems presumably containing organocopper[36] compound or organosilver compound[37] as an intermediate have been studied. Some of these systems, e. g., $AgNO_3$-$Pb(C_2H_5)_4$[38], were found to be fair catalyst for vinyl chloride polymerization. As organosilver compound is unstable, the polymerization is considered to be initiated by radical formed on account of the Ag-C bond decomposition.

Section 9. Group IIb Element (Zn, $\chi = 1.5$; Cd, $\chi = 1.4$; Hg, $\chi = 1.9$)

Of the elements of this group, alkylmercury behaves quite differently from the other two; the former is very stable to water and oxygen, the latters being spontaneously inflammable in air and violently

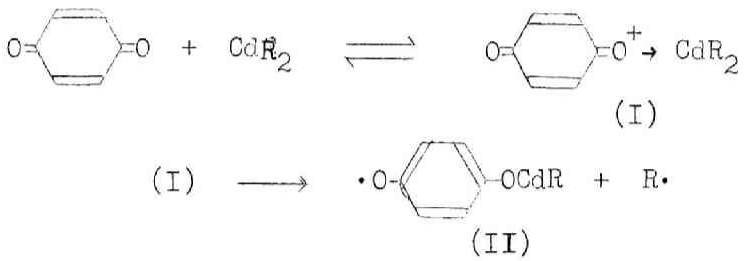
decomposed by water.

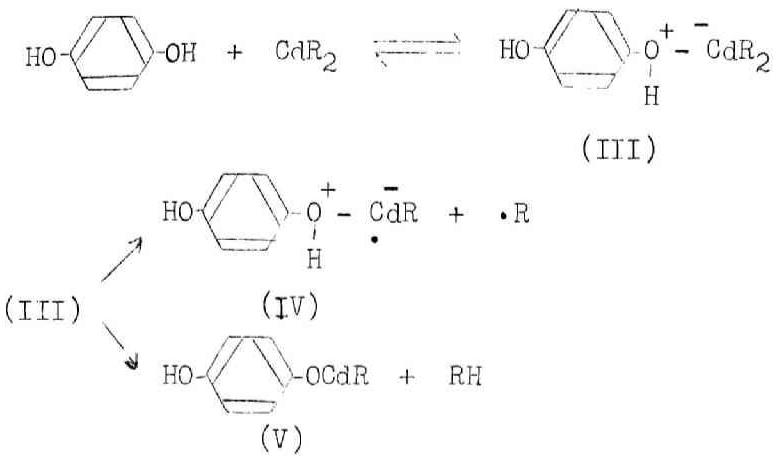
Zinc- and cadmium-alkyl themselves show no catalytic activity for vinyl polymerization unless any cocatalysts are used. Alkylzinc was utilized for the polymerization of ethylene and propylene by itself or as mixed catalyst[10,23], however, it was not good catalyst, giving polymer with low stereospecificity.

Zinc- and cadmium-alkyls can be fair initiators for vinyl polymerization when molecular oxygen is present as cocatalysts (Chapter 6, ref. 29). Initiation mechanism is considered just like as in the case of boronalkyl catalyzed polymerization. Some details were investigated by Yukio Nakayama[20] on alkylzinc-oxygen system catalyzed vinyl polymerization. Intermediate organometallic peroxide was isolated by the reaction of alkylzinc with oxygen at low temperature and was proved to have strong catalytic action in the polymerization.

Besides the cocatalytic action of oxygen to zinc- and cadmium-alkyl, some quinones and phenols were found to have excellent cocatalytic action[29].

A possible mechanism for the cocatalytic action of quinones and phenols upon the polymerization, for example, was assumed as follows:





In this mechanism an unstable addition compound (I) or (III) which is formed by one electron transfer from oxygen to cadmium was assumed. These adducts may rapidly decompose to give alkyl radical which induce the polymerization of vinyl monomers.

The cocatalytic action of quinones and phenols was also found in the cases of zinc- and aluminum-alkyls.

It is very interesting that these radical inhibitors have co-catalytic activity in the case mentioned above. These 'cocatalyst' present in an excess quantity exhibited an inhibitory action.

To the trialkyl-boron or -antimony catalyzed polymerization, either of quinone and hydroquinone exhibits only an inhibitory action.

Differently from zinc and cadmium, mercury alkyl has no catalytic activity for vinyl polymerization by itself in the dark or even in the presence of oxygen (Chapter 4). Reported activity of alkylmercury[31] may be interpreted in terms of radical decomposition of carbon-mercury bond, the strength of which is rather small.

Each alkyl of the element of this group has a linear molecular structure. The great difference of alkylmercury from the other metal

alkyl of this group may be accounted for by much higher electronegativity of mercury than the other two. High electronegativity of the metal may hinder electron transfer from oxygen atom.

Binary systems composed of metal alkyl of this group and transition metal halide were utilized for olefin and diolefin-polymerization, and in some cases stereospecific polymer was obtained, though with not so high yield[39]. These systems were examined also for vinyl polymerization, and they were found excellent initiators, when the two components were mixed in the presence of the monomer (Chapter 5). The polymerizations are considered to proceed by a radical mechanism.

Section 10. Organometallic Compound of the Transition Metal

Alkyl compounds of transition metal are very unstable, and has not yet been isolated except for a few compounds*).

Halides of titanium, vanadium, chromium or nickel are often used as cocatalyst with organic compounds of metals of groups I, II and III. In these cases there would be formed some organic compounds of transition metal. True reaction species which is effective in the Ziegler type - catalyzed olefin polymerization, however, would be very complicated, though there have been appeared a large number of investigations in this field. Some discussions on this point will be made in the

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*) Cyclopentadienyl or aromatic titanium compound; and alkyltitanium trichloride[40,41,42].

following section, taking the writer's results into account.

Section 11. Classification of Organometallic Compound as Catalyst for Vinyl Polymerization

It will be reasonable from the foregoing discussion to consider that the catalytic nature of the organometallic compound is classified into six types, where RM and MX imply organometallics and metal halide, respectively :

A) Anionic polymerization

$$MR + CH_2=CHX \longrightarrow R\text{-}CH_2\text{-}\overset{+}{M}\overset{-}{C}HX \longrightarrow$$

B) Oxygen-cocatalyzed radical polymerization

$$MR + \text{O-donor} \longrightarrow M\text{-}O\text{-}O\text{-}R \longrightarrow MO\cdot + \cdot OR \xrightarrow{CH_2=CHX} RO\text{-}CH_2\text{-}CHX\cdot \longrightarrow$$

C) Coordinated anionic polymerization by RM-MX system

$$MR + M'X \longrightarrow \underset{\text{(complex)}}{RM \cdot M'X} \xrightarrow{C=C} \overset{C\cdots C}{RM \cdot M'X} \longrightarrow$$

D) Radical polymerization by RM-MX system

$$MR + M'X \xrightarrow{CH_2=CHX} M'R + MX + R\text{-}CH_2\text{-}CHX\cdot \quad \text{etc.} \longrightarrow$$

E) Polymerization by radical decomposition

$$MR \longrightarrow M\cdot + R\cdot \longrightarrow R\text{-}CH_2\text{-}CHX\cdot \longrightarrow$$

F) Lone-pair initiated anionic polymerization

$$MR + CH_2=CHX \longrightarrow \overset{+}{M}(R) - CH_2 - \overset{-}{C}HX \longrightarrow$$

Table III shows a classification of organometallic compound as catalyst for vinyl polymerization.

Table III. Classification of Organometallic Compounds as Catalyst for Vinyl Polymerization

	Ia	IIa	IIIb	IVb	Vb	VIb	VIIb	VIII			Ib	IIb	IIIa	IVa	Va	VIa	VIIa	O
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	A
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

Compound group \ Reaction type	A	B	C	D	E	F
1	+	-	+	-	-	-
2	+	+	+	-	-	-
3	-	+	+	+	-	-
4	-	+	-	+	-	-
5	-	-	+	+	+	-
6	-	-	-	-	-	+

+ : Polymerization. - : No polymerization.

As shown in the table organometallic compounds are classified into

six groups according to their catalytic nature, the types of which were mentioned above.

Metal alkyl, RM, can induce the anionic polymerization (A) when the metal, M, belongs to groups I_a and II_a in the periodic table (Groups 1 and 2). Among these, the compounds of the metals with comparatively large electronegativity, Li, Mg, and Be, are also capable of initiating polymerization of mechanism (B) under a certain condition (Group 2).

Alkyl compounds of the other metals cannot induce the vinyl polymerization by themselves, unless the C-M bond-strengths in these compounds are weak enough to break (E) under the influence of heat or light (Group 5: Hg, Pb). From such a point of view it may be reasonable to consider that we can expect type (E) reaction in most of the organometallic compounds to some extent.

The writer considers, as mentioned previously, that the organometallics catalyzed anionic polymerization proceeds by 1,4-addition of the propagating organometallics to α,β-unsaturated carbonyl (or cyano) group. As studied by Gilman[2], some organometallics other than those of groups I_a and II_a elements are also capable of 1,4-addition to α,β-unsaturated carbonyl bond. However, the addition product may be too stable to induce further addition reaction, i. e., propagation, because of the larger electronegativity of the metal or rather covalent nature of enolate-metal bond of the product.

M = Group I_a, II_a; $\quad C=C-C=O \xrightarrow{R-M} R-C(C=C=O)^{-}M^{+}$

M = Others ; $\quad C=C-C=O \xrightarrow{R-M} R-C-C=C-O-M$

This difference may lay the distinguishable boundary observed between Group 1 or 2 metals and the others.

Groups 3 (Al, Zn, Cd) and 4 (B, Sb, Bi) compounds are characterized by reaction (B). All of these organometallic compounds are very sensitive to oxygen, some of them being spontaneously inflammable in the air. This property enables reaction (B).

Ziegler type reaction (C) is very common in a wide variety of organometallic compounds. However, this type of catalyst is effective only for non-polar monomers such as olefin and diolefin. For the polymerization of vinyl compounds the catalyst complex showed only poor activity. Reaction (D) is rather common in vinyl polymerization by such a system (Chapter 5).

Section 12. On the Nature of Ziegler-Natta Type Catalyst

As mentioned above, Ziegler-Natta type catalyst seems to have dual character, depending on the kind of monomer.

In general, catalyst systems utilized in 'coordinated anionic' olefin polymerization are heterogeneous and polymerization proceeds rather slowly at relatively high temperature. In this case transition metal M' of lower valence, reduced by RM, in the catalyst complex plays an important role. The repetition of reaction of the M' with olefin (alkylation of M') results in the olefin polymerization and the reaction at the surface of the heterogeneous complex enables the formation

of stereospecific polymer. It is quite natural to consider some 'coordination' in the reaction, considering the stereospecificity.

On the 'anionic' nature of the Ziegler catalyzed olefin polymerization, there are considered to exist some problems left. According to the studies of the polymerization of styrene derivatives by this type catalyst, styrene derivative with the substituent of lower σ-value shows higher activity to the polymerization[43]. This fact may indicate the reaction to proceed rather by a cationic mechanism. This may be explained by the easiness of adsorption of these monomers to the catalyst complex, especially to the 'Lewis acid' component -- transition metal -- of the complex. The writer considers, however, the adsorption itself to be an initiation reaction.

In connection with the fact mentioned above, Kargin[44] found interesting behavior of titanium trichloride, which can induce the styrene polymerization in a molecularly dispersed state. In crystalline state the chloride shows no activity. Kargin assigned the activity to the defectful structure of the molecular dispersed titanium chloride. The role of organometallic compounds in Ziegler catalyst may partly be considered to react with transition metal halide, as 'reducing agent' in the words often used, to form a complex with such a structure having many defects. The defect may be related to unfilled d-electron shell, which was exposed on account of the 'reduction' by the organometallic component of the catalyst system. In fact, transition metal halide (Group IIIb -- VIII) show generally high activity, whereas non-transition metal halide has no activity as a component for

Ziegler catalyzed olefin polymerization. On the contrary, for the vinyl polymerization by metal alkyl -- metal halide system the halide of non-transition metal also is effective cocatalyst. In the latter case the easiness of the transfer reaction of alkyl group or the like between organometallics and halide of the system is more important. Superiority of vanadium compounds in activity compared with titanium halides may be explained by the fact that the former is more easily alkylated than the latter[45]. The difference in the stereospecificity of the catalyst complex with respect to the organometallic compound may be accounted for by the regularity of the complex formed. There may exist two kinds of active center on the catalyst complex: One has regular structure, forming stereoregular polymer; the other has irregular structure, forming non-stereospecific polymer.

As to the stereoregulated polymerization of propylene, Natta[19] suggested that the best organometallic component is the alkyl of lithium, beryllium or aluminum, all of which are small in ionic radius, and this fact may be related to the stereoregularity of the catalyst complex.

On detailed mechanism of stereospecific reaction of the system there have been proposed a large number of hypotheses. However, no definite conclusion has been achieved as yet.

Although the catalyst complex prepared in the absence of the vinyl monomer generally shows low catalytic activity for the polymerization, there are some patents on the polymerization of polar vinyl monomers by Ziegler-Natta type catalyst, in which the preparation of crystallizable poly(methyl methacrylate)[46], poly(vinyl chloride)[46] or

poly(vinyl acetate)[47] is described.

In these patents, the use of some 'complexing agents' is described in combination with organometallics and metal halides. The complexing agent includes ether, amine or other 'electron donors' which form complex with the catalyst and prevent the side reactions of the polar group of the monomer.

However, there are few reports except for the patent literature. Only Etlis and Minsker[48] reported the preparation of crystalline poly(vinyl chloride) by aluminum alkyl -- titanium trichloride system using some complexing agents. The mechanism of the reaction, however, is still obscured.

At elevated temperatures, radical decomposition of the catalyst complex also seems to take place (cf. Chapter 5, Table VIII). The formation of crystalline poly(vinyl chloride) cited above was effected under such a condition and may be considered to proceed through a kind of 'coordinated radical' polymerization mechanism.

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CONCLUSION

In this paper some detailed investigations on the catalytic nature of some organometallic compounds were described and a general survey of the reactivity of organometallics in this connection was planned.

In contrast to the ambiguous concept in the organometallics-catalyzed polymerization in the earlier stage of this research, the polymerizations were found to proceed not always by an anionic mechanism. Different mechanisms were made clear in cases of different organometallics; anionic in some cases, radical in the others. Anionic polymerization is observed only when the organic compound of group I_a or II_a metals is used as catalyst. In the other cases there were found various types of radical polymerizations.

The most interesting in practical and theoretical field is anionic type catalyst, which can afford stereospecific polymer. The kind of central metal atom or organic group has been known to show important effect on the stereospecificity of the polymerization reaction. Even polymers of completely different molecular structures were obtained from a certain monomer by different catalysts of this type under suitable conditions.

Together with the formation of stereospecific polymers by cationic catalysts and Ziegler type catalysts, organometallic catalyzed

anionic polymerization supply us the most interesting field of organic chemistry. Stereospecific reactions on heterogeneous or coordinated catalyst systems resulting in the formation of stereoregular polymer is reminiscent of specific enzymatic reactions in biochemistry.

Stereospecific polymers formed by these catalysts have many specific properties, in solid state or in solution, and may be utilized as a reagent for some specific reactions, which case again remind us of biochemical reactions.

Once the preparative method of stereoregulated polymer was established, the developement of this field will be made in the future in the application of the product for some specific reactions as suggested above; that is, a gate to a new field of elaborate organic chemistry.

In this field as well as in theoretical field organometallic compound will find new interesting utilities. Organometallics and their relatives has now been utilized for the polymerization of the monomers other than olefins, diolefins and vinyl compounds; i. e., aldehydes, olefin oxides or other heterocyclic compounds. Here again stereospecific behavior of some organometallics was found.

Although the problem of stereospecific reaction, including the reactions other than polymerization, is very complicated and requires further intensive work, this problem is, and will be, the most attractive problem of organic chemistry.

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No.		Relating Chapter
1	Triethylboron as Initiator for Vinyl Polymerization. J. Furukawa, T. Tsuruta, and S. Inoue J. Polymer Sci. 26 (1957) 234.	(1)
2	Vinyl Polymerization catalyzed by Triphenyl- or Tribenzyl-boron. J. Furukawa, T. Tsuruta, and S. Inoue Paper presented at 11th Ann. Meeting of Chem. Soc. of Japan, (Tokyo, Apr., 1958), Abstract, p. 97.	(1)
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